Faculty of Health, Engineering and Sciences

Application of electro-kinesis for saline-sodic irrigation management

A Thesis submitted by

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For the award of

DOCTOR OF PHILOSOPHY

2016

I dedicate this work to

My Mother

My Father’s soul

My Wife

My Children

My Siblings

My whole Family

And all of my Friends

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USQ, Queensland, Australia.

Abstract

The increasing demand for food production, and scarcity of good quality water with which to address this, has led to the use of marginal quality water, such as saline-sodic groundwater, for irrigation purposes, particularly in the arid and semi-arid areas. Long-term use of saline–sodic water for irrigation may adversely affect soil properties and crop yields. Traditionally, larger amounts of irrigation water are applied to leach salts from the root zone in order to maintain the root zone concentration of salts below the threshold for plant damage. However, the addition of excess water for salt leaching may lead to nitrate leaching out of the root zone, degrading groundwater quality and reducing crop production. To reduce these issues, this research has evaluated the potential for electro-kinesis (EK) to manage nitrate and salts within a simulated root zone depth (sand column) irrigated with saline-sodic water.

While previous research has been undertaken to evaluate the use of electro-kinesis (EK) under a narrow range of soil conditions, there is a lack of data on the ability to simultaneously control salt and nitrate movement in soil using EK, and insufficient evidence to understand the soil, water and management conditions under which EK may be usefully applied to improve root zone management. Therefore, three laboratory trials were conducted using sand columns (uncharged particles) investigate the effect of EK on salt distribution, nitrate movement and management options for the use of EK in combination with saline-sodic irrigation. A combined soil-water and EK model was subsequently developed and validated. The model was then used to predict nitrate and salt distribution under a range of EK and irrigation treatments.

The first study evaluated the effect of applying EK to irrigated sand columns (30 and 50 cm) with two different electrode separate distances (20 and 40 cm, where the anode was installed at the top while the cathode sheet was installed at the bottom of the sand column). The results showed that EK application significantly affected both soil solution ion movement within the column and the soil pH near the electrodes. Anions (i.e. chloride) were moved upwards in the sand column and held in the upper layers against the downward flow of applied irrigation water. However, the magnitude of the effect varied as a function of the EK application period, rate of EK application and the distance between the electrodes.

The second trial evaluated nitrate movement with three EK treatments (0, 0.005A, 0.01A and 0.02A, for 24h) applied to sand columns under various irrigation rates (0, 10, 20 and 30 mL h^{-1} for 9h). The results showed that application of EK resulted in a significant increase in nitrate concentration near the anode, and a significant decrease near the cathode. At the same time, the EC was significantly increased and the solution pH became more acidic (<6.5 initial condition) near the anode and alkaline (~ pH 10) near the cathode. Irrigation significantly decreased the nitrate concentration throughout the sand columns with leaching increasing as high irrigation rates and longer irrigation durations were applied.

The third experiment evaluated the effect of applying 0.01A EK for 24 h on both sodium and nitrate movement in a sand column. The results demonstrated the potential to move nitrate upwards in the sand column while simultaneously moving sodium downwards. Substantial changes in nitrate concentration were observed, with increases recorded near the anode and a reduction observed near the cathode. The sodium concentration increased near the cathode and decreased near the anode.

Abstract

The sequential application of EK, irrigation and fertigation was shown to be an effective strategy for managing the movement of water and solution in a sand column. In general, nitrate moved upwards and sodium moved downwards during EK application. The application of irrigation and fertigation buffered the effects of EK on pH and EC. Periods of drainage also allowed for redistribution within the column by both diffusion and hydraulic movement under gravity. However, the dynamic responses and time-lag associated with changes at each depth in the root zone make it difficult to identify optimal management strategies. Hence, a numerical model incorporating the effect of both soil-water movement and EK on the movement and distribution of ions would be beneficial.

A combined "Diffusion Convection Electro-osmosis Electro-migration Model" (DCEEM) was developed and validated using experimental data. The model was shown to accurately predict soil-water content, nitrate movement and salt concentration. This model was then used to simulate alternate EK and irrigation management strategies and demonstrate the effect of these management practices on EC changes, soil-water and nitrate movement within irrigated sand columns. Although the current version of the model has limitations including the selection of system design and management options, the results confirmed the utility of the model to better understand the relative scale and nature of the soil-water and ion movement interactions within the column. Recommendations to improve the model and thus the ability to determine best management practices for a range of system requirements were provided.

Certification of Thesis

This thesis is entirely the work of ***Jamal Mohamed Fernana*** except where otherwise acknowledged. The work is original and has not previously been submitted for any other award, except where acknowledged.

Student and supervisors signatures of endorsement are held at USQ.

Professor Steven Raine

Principal Supervisor

Dr John Bennett

Associate Supervisor

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List of symbols and abbreviations

A	Cross-sectional area of soil tube (m^2)
C	Concentration of ions in (mol L^{-1}) or (C m^{-3})
CEC	Cation exchange capacity ($cmol_c$ kg^{-1})
C_i	Concentration of species i (moles m^{-3})
D	Dielectric constant of the pore fluid (F m^{-1})
D^*	Diffusion coefficient (m^2 s^{-1})
D_{eff}	Effective diffusion coefficient in soil (m^2 s^{-1})
E	Electric field gradient (V m)
ε	Soil electrical permittivity (C^2 $N^{-1}.m^{-2}$)
EC	Electrical conductivity (dS m^{-1})
EC_{iw}	Electrical conductivity of irrigation water (dS m^{-1})
ESP	Exchangeable sodium percentage
F	Faraday constant (C mol^{-1})
H	Hydraulic head gradient
H^+	Hydrogen ion
I	Current through soil column (A)
J	Current density (A m^{-2})
J_d	Ion flux due to diffusion (mol m^{-2}. s^{-1})
J_i	Total Flow rate of specific ion (mol $m^{-2}.s^{-1}$)
J_m	Migration flux of salt ions (mol $m^{-2}.s^{-1}$)
K_e	Coefficient of electro-osmosis permeability (m^2 $V^{-1}.s^{-1}$)
K_h	Hydraulic conductivity (m s^{-1})
LSD	Least significant difference
OH^-	Hydroxyl ion
Pb	Bulk density (g cm^{-3})

List of Symbols

Q_e	Water flow rate (m^3s^{-1})
Q_w	Electro-osmosis flow rate ($m^3\ s^{-1}$)
R^2	Coefficient of Determination
SAR	Sodium adsorption ratio
ζ	Zeta potential (V)
η	Viscosity of the pore fluid ($N.s\ m^{-2}$)
μ	Mobility of ions in the electrolyte solution ($m^2\ V^{-1}.s^{-1}$)

Chapter 1: Introduction

1.1 Background

The need for increased food production is important due to the growing world population. For example, to maintain food supply at the current level, global food production needs to increase by 38% by 2025 and by 57% by 2050 (Wild 2003). Irrigation has played a major role in supporting agricultural production, particularly in arid and semiarid regions of world, and this role is likely to become more important as the demand for food increases. However, there is a growing shortage of suitable water for agriculture due to environmental requirements, increased variability and changes in rainfall, as well as the increasing and competitive demand for water by urban and non-agricultural industries. Hence, the focus has shifted towards exploring the feasibility of alternative sources of irrigation water. More recently, marginal quality water such as saline-sodic groundwater and industrial effluent has been used for irrigation (Fereres & Soriano 2007; Pereira et al. 2002).

Long-term use of untreated saline–sodic water for irrigation may adversely affect soil properties and crop yields (Bajwa & Josan 1989; Ezlit 2009; Manchanda et al. 1982). However, irrigation using marginally saline-sodic water when managed on a soil specific basis is feasible (Bennett 2011; Bennett & Raine 2012a; Chi et al. 2012; Ezlit et al. 2013; Quirk & Schofield 1955). Where the application of saline-sodic irrigation water is not managed, or incorrectly managed, negative impacts on soil productivity and soil structural integrity occur due to sodification (So & Aylmore 1993; Sumner 1993). Salinisation may also decrease plant water uptake due to an osmotic effect, although this same effect may stabilise soil structure, even where sodic (Ayers & Westcot 1985; Brinck & Frost 2009; Cucci et al. 2015; Mamedov & I 2014).

Excessive soluble salts and sodium concentrations in the soil solution may also cause osmotic stress and specific ion toxicity which influence the plants' uptake of nutrients (Alharby et al. 2014). In particular, soil salinity may affect crop total nitrogen uptake and has a negative effect on biological activity and the nitrogen balance in the soil (Van Hoorn et al. 2001; Vaughan & Letey 2015).

Increasing the sodium concentration within the root zone may produce indirect impacts on plant growth due to its effect on soil structure, density and soil water relations resulting in low plant available water capacity and hydraulic conductivity (Ezlit et al. 2010; Vance et al. 2008). However, these impacts can be alleviated by improvements in land and water management (Tavakkoli et al. 2010).

Electro-kinesis (EK) involves applying an electrical current (or voltage) across a porous media (e.g. soil). The electrical current generates an electrical field which transports charged particles, free ions and water through the porous media (Probstein & Hicks 1993). The main processes involved in this technology are electro-migration and electro-osmosis. Electro-migration is the transport of charged ions in solution (Probstein & Hicks 1993). Electro-osmosis is defined as the mass flux of pore fluid and charged particles under an electric field (Acar et al. 1995) where the electric field surrounding the charged particles controls attraction and repulsion (Valkenburgh 1995). The electric field is a vector field with magnitude and direction at every point in space. The ability of an electric field to transport ions through porous media has led to researchers studying the use of EK to remove contaminates from soils.

EK has been used to extract heavy metals, organic compounds and remove inorganic matter from soils. For example, Van Doren and Bruell (1987) investigated the use of an electrical treatment to remove benzene from a water saturated clay with low hydraulic conductivity. This study showed that the benzene was completely removed from the clay after two weeks of the electrical treatment. Similarly, Acar et al. (1994) showed that approximately 90-95 % of cadmium (II) in a saturated kaolinite could be removed by EK. Furthermore, Kim et al. (2001) investigated EK as a remediation method to remove lead (Pb) and cadmium (Cd) contaminants from kaolinite and a tailing-soil. They found that approximately 75-85% of both Pb and Cd were removed from the kaolinite and 50-70% from the tailing-soil after application of EK for 4 days. Jeon et al. (2015) investigated the potential for an in situ EK system to remove arsenic (As), copper (Cu) and Pb from a contaminated paddy rice field. They found that approximately 44% of the As, 40% of the Cu and 47% of the Pb were removed from the soil after 24 weeks of applying EK.

The ability of EK to control nitrate movement has also been studied. In a lysimeter test, Cairo et al. (1996) evaluated the effect of using EK to concentrate and remove nitrate from soil using horizontal drainage tubing and parallel electrodes. After applying a small electrical current to a saturated soil, the nitrate concentration was found to increase towards the cathode due to a hydraulic effect. However, in an unsaturated soil, the nitrate was found to migrate towards the anode. Eid et al. (2000) evaluated the ability of EK to maintain nitrate near the anode in a saturated sandy soil under both closed and open system conditions. In both systems, the nitrate was concentrated and retained near the anode. Jia et al. (2006) studied the effect of applying an electrical current to control nitrate movement and pH changes in a vertical column of partially saturated sandy soil. They found that the highest nitrate concentration was recorded within 5 mm of the anode when 80 mA current was applied for 6 hours while the lowest concentration was measured near the cathode. Significant pH changes were also observed with the lowest pH (pH=3.5) measured at the anode and the highest (pH=11) measured at the cathode.

Researchers (e.g. Choi et al. 2009; Eid et al. 2000; Jia et al. 2005) have studied the potential to use EK to either remove salts from the root zone or to control nitrate movement under a narrow range of` soil conditions. However, there is a lack of data on the ability to simultaneously control salt and nitrate movement in soil using EK and insufficient evidence to understand the soil, water and management conditions under which EK may be usefully applied to improve root zone management.

EK has the potential to improve the management of salt and nitrogen within irrigated root zones, particularly where saline water is applied. However, to enable this technique is to be effectively deployed and managed in a commercial irrigation system there is a need to develop appropriate EK management strategies to maintain nitrate and minimise salt concentrations within the root zone. Hence, this research will evaluate under laboratory conditions, the potential for EK to assist in managing salinity and nitrate movement in soils irrigated with saline water.

1.2 Overview of research

1.2.1 Research hypotheses

This thesis is based on the following hypotheses:

- Excess salts contained within irrigation water or the soil can be removed from the root zone by application of electro-kinesis.
- Electro-kinesis can be used to manage the movement of nitrate (NO_3^-) within the root zone.
- Electro-kinesis can be used to simultaneously improve nitrate retention and salt drainage in a sandy soil irrigated with saline-sodic water.
- Options for using EK and irrigation applications to control salt and nitrate movement can be evaluated by using a soil-water model incorporating EK.

1.2.2 Specific objectives of research

This project aims to evaluate the potential use of electro-kinesis as a management strategy for controlling nitrate movement and reducing the impact of saline-sodic irrigation water within a root zone. The main objectives of this research are:

- Evaluate the efficacy of using electro-kinesis to increase salt drainage from an irrigated sand column
- Evaluate the potential use of electro-kinesis to retain nitrate within an irrigated sand column.
- Evaluate the use of EK to simultaneously manage nitrate retention and salt drainage in an irrigated system with saline-sodic water applied.
- Develop a combined soil-water and EK model and use the model to demonstrate the effect of management variables on the ability to control nitrate and salt movement in an irrigated soil.

1.3 Structure of dissertation

This dissertation contains eight chapters (Figure 1.1). Chapter 2 provides a brief review of the effects of irrigation with saline-sodic water on soil properties and plant growth. It also provides a general review of electro-kinesis processes, theories and applications, including the effects of EK on ion movement in soils.

Chapter 3 describes the general materials and methods used in this research. Chapter 4 reports on an experiment to evaluate the efficacy of using electro-kinesis to remove salts from an irrigated sand column. The potential use of electro-kinesis for controlling nitrate movement in an irrigated soil column is then evaluated (Chapter 5). Subsequent research (Chapter 6) then evaluated the ability to simultaneously manage nitrate and salt movement in a sand column irrigated with saline-sodic water. Chapter 7 provides an outline of the EK-hydraulic model and uses the model to evaluate strategies for controlling salt and nitrate movement with irrigation. Chapter 8 provides a general conclusion and recommendations for further research.

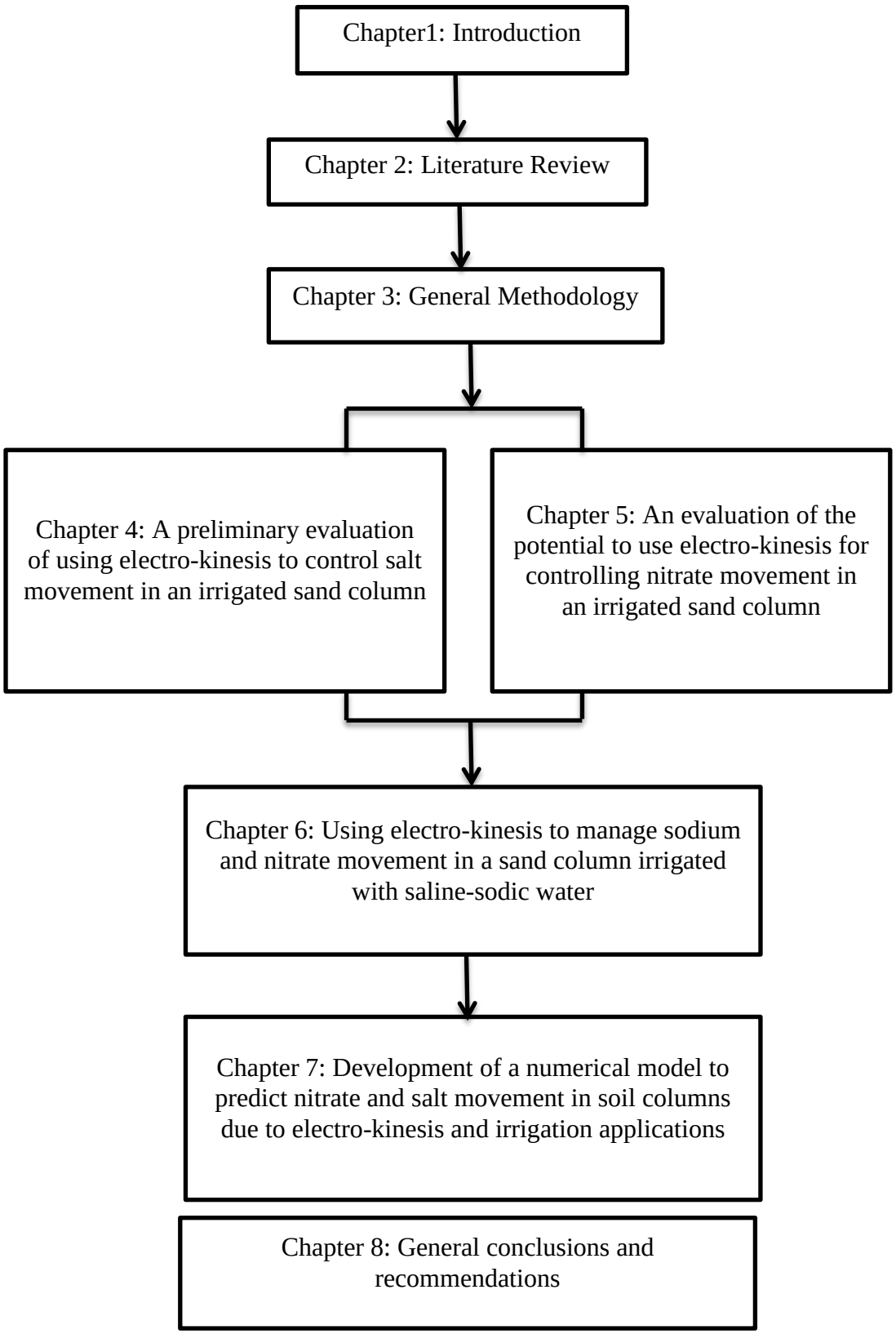

Figure 1-1 Outline of dissertation structure

Chapter 2: Literature Review

2.1 Introduction

This chapter describes specific impacts related to the use of saline-sodic water on irrigated soil and plant growth. It also provides a general review of the electro-kinesis processes, theories and applications, as well as the justification for undertaking this research. Section 2.2 discusses water quality and the problems associated with the use of low quality (saline-sodic) water on irrigated soil. Section 2.3 provides brief information on soil-water potential. The plant salt tolerance is discussed in section 2.4. Section 2.5 provides concise discussion regarding to traditional management of irrigation with saline-sodic water. Section 2.6 presents the electro-kinesis (EK) processes and theories including the use of EK to remove contaminates from a soil, and introduces the potential application of EK in agriculture as a soil management method for removing excess salts and maintaining nitrate in the root zone.

2.2 Irrigation water quality

Water used for irrigation always includes different dissolved salts (Ayers & Westcot 1985). The types and amounts of salt in the water may lead to negative impacts on both crop yield and soil properties. Increasing the salt concentration in soil solution affects plant water uptake due to the changes in soil water potential (i.e. osmotic potential) (Hadas 1976). Therefore, water quality is a major factor when determining the suitability of water for use in irrigation. The basic criteria need to categorise water for irrigation include: (1) water salinity or total dissolved salt (TDS); (2) Sodium Adsorption Ratio (SAR); (3) acidity (pH) and alkalinity (i.e. carbonate and bicarbonate), and; (4) the concentration of elements toxic to plant growth (Bauder et al. 2011).

2.2.1 Salinity

Salinity has been defined as the sum of mass concentration of dissolved ions in the water (Burger & Celkova 2003). The major dissolved inorganic ions in water are generally Na^+, Ca^{2+}, Mg^{2+}, K^+, HCO_3^-, SO_4^{2-} and Cl^-. The total dissolved salt (TDS) in irrigation water is often assessed by measuring its electrical conductance (EC) and the common units used are mS/cm, dS/m or µS/cm. The salinity of the applied irrigation water affects the soil salinity.

A salinity problem occurs when the level of salt in the irrigation water is high enough to cause the salt concentration in the soil solution to exceed the crop threshold level (Maas, E. & Hoffman, G. 1977). At this level of salinity a crop will be unable to extract the required water from the soil solution. As a result, plant growth slows and starts to develop drought symptoms (Ayers & Westcot 1985). The long term use of this type of water in irrigation with mismanagement can increase the potential for soil degradation and limit crop production (Simsek & Gunduz 2007). Hence, the guidelines are used to evaluate water quality to determine the suitability of water for use in irrigation. Soil and water salinity criteria based on the plant salt tolerance grouping is presented in Table 2-1 (ANZECC 2000).

Table 2-1: General guidelines for salinity of irrigation water (ANZECC 2000 adapted from DNR 1997b)

Plant salt tolerance groupings	Water or soil salinity rating	Average root zone salinity, EC_{se} (dS/m)
Sensitive crops	Very low	<0.95
Moderately sensitive crops	Low	0.95-1.9
Moderately tolerant crops	Medium	1.9-4.5
Tolerant crops	High	4.5-7.7
Very tolerant crops	Very high	7.7-12.2
Generally too saline	Extreme	>12.2

2.2.2 Sodicity

Sodicity, also known as the sodium adsorption ratio (*SAR*), is the most common quality factor used to determine the sustainable use of irrigation water particularly on clay soils. The *SAR* value of irrigation water quantifies the relative concentration of sodium (Na^+) to calcium (Ca^{2+}) and magnesium (Mg^{2+})(Ayers & Westcot 1985):

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{+2}]+[Mg^{+2}]}{2}}} \qquad \text{Equation 2-1}$$

where $[Na^+]$, $[Ca^{2+}]$ and $[Mg^{2+}]$ are expressed in $mmole_c$ /litre (ANZECC 2000).
The stability of clay soils is affected by the interaction of the EC_i and SAR. A generalised relationship is shown in Figure 2-1 (ANZECC 2000).
High levels of SAR in irrigation water result in an increase in the soil sodium level, known as the Exchangeable Sodium Percentage *(ESP). ESP* is defined as the ratio of exchangeable sodium percentage (cmolc kg^{-1}) to the total cation exchange capacity of the soil CEC (cmolc kg^{-1}). The ESP is calculated as:

$$ESP = \frac{Na \times 100}{CEC} \qquad \text{Equation 2-2}$$

where Na is concentration of sodium (cmolc kg^{-1}) in soil, and CEC is the cation exchangeable capacity (cmolc kg^{-1}).

Increasing rates of Na^+ in soil solution affects soil structure, infiltration rates, drainage rates and crop growth potential (Ayers & Westcot 1985).

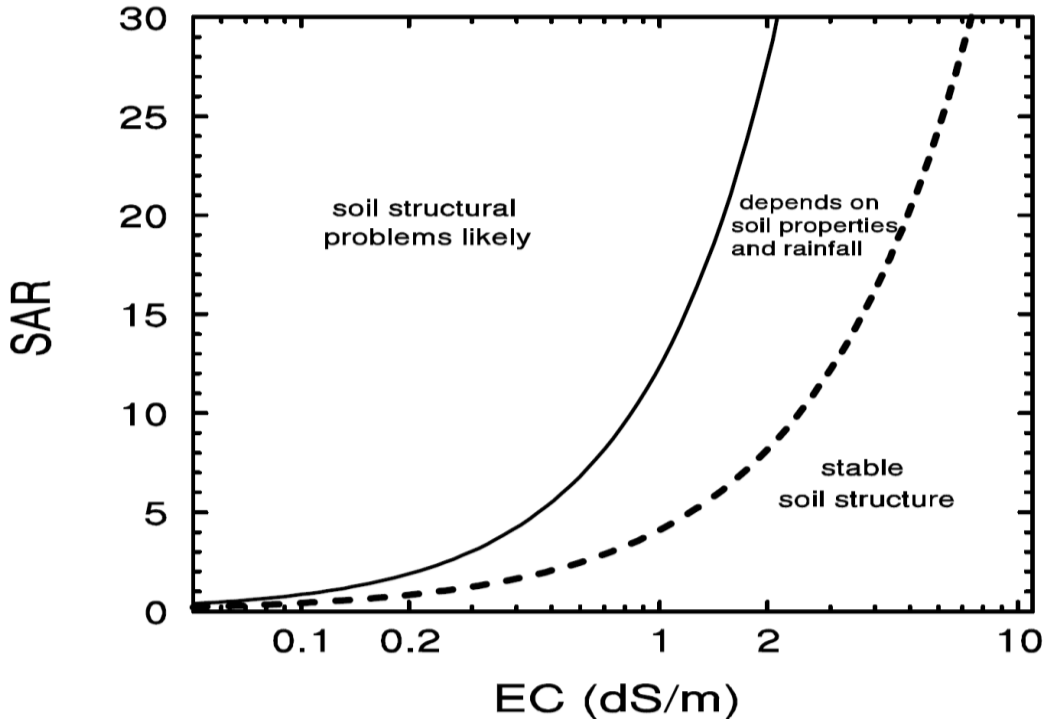

Figure 2-1: Effect of irrigation water SAR and EC on the stability of soil structure (ANZECC 2000 from DNR 1997a)

There is close relationship between SAR of irrigation water and the resulting ESP. Therefore, the ESP can be calculated from SAR (Richards 1954).

$$ESP = \frac{100(-0.0126 + 0.01475SAR)}{1 + (-0.0126 + 0.01475SAR)}$$

Equation 2-3

2.2.3 Acidity and Alkalinity

The term pH, which is the negative log of the concentration of hydrogen ions, refers to acidity and alkalinity of irrigation water. The range of pH value has been divided into three parts: acid (pH<7); neutral (pH=7) and; alkaline (pH>7). The typical value of pH for irrigation water is from 6.5 to 8.4 (Bauder et al. 2011). The pH has significant impact on plant nutrition due to its effect on nutrient availability (Tu & Ma 2003). Values of pH that are higher than 8.5 are often caused by high bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) concentrations. High concentrations of carbonate ions create insoluble salts from calcium and magnesium ions leading to a proportionally higher sodium concentration (i.e. *SAR*) in the soil solution (Bauder et al. 2011). The higher *SAR* may influence crop yield and soil properties (Section 2.2.2).

2.3 Soil-water potential

Soil provides plants with nutrients, water and air. The plant availability of water in the soil is controlled by two important characteristics; the amount of water in the soil and the forces holding the water in the soil. Generally, the amount of water in soil has an impact on many processes in the soil such as gas exchangeable, the movement of nutrients to plant roots, soil temperature and water absorption (Jury 2004). Furthermore, water potential also plays a major role in water flow within the soil. Therefore, investigating water potential and water content is very important to improve understanding of the soil-plant-water relationship.

The term water potential (ψ_w) is defined as the amount of energy required to move the unit of water in the soil-water equilibrium system to a reference point at same temperature (Hanks & Ashcroft 1980). Under equilibrium conditions, water moves from the point that has high total water potential to the point that has low total water potential (Hanks & Ashcroft 1980). Total water potential includes gravitational potential (ψ_z), matric potential (ψ_m), solute potential (ψ_s) and pressure potential (ψ_p).

$$\psi_w = \psi_z + \psi_p + \psi_m + \psi_s \qquad \textbf{Equation 2-4}$$

where:

Gravitational potential (ψz) is defined as the difference in elevation of an infinitesimal amount of pure and free water and the reference point to the soil water (Hanks & Ashcroft 1980; Jury 2004);

Matric potential (ψ_m) is formally defined as the energy per unit volume of water needed to transfer a small amount of water from a reference soil-water pool to any selected point in the soil at reference air pressure (Jury 2004)

Solute potential (ψs) is '*the change in energy per unit volume of water when solutes identical in composition to the soil solution at the point of interest in the soil added to pure, free water at the elevation of the soil*' (Jury 2004, p. 54).

Pressure potential (ψ_p) is defined as the water pressure applied by saturated water on the selected point in the soil (Jury 2004).

2.4 Plant salt tolerance

Salt tolerance is defined as the plant's ability to survive and provide economic production under a salinity stress (Bresler 1982). Salinity influences plant growth and yield through both osmotic and toxic (specific ion) effect. Therefore, plants have evolved several of biochemical and molecular strategies either to exclude salt from their cells or to tolerate its presence inside the cells (Ingram & Bartels 1996). Some of these strategies are selection or exclusion of ions, control of ion uptake by roots, synthesis of compatible solutes and induction of anti-oxidative enzymes (Parida & Das 2005).

The general salt tolerance of crops has been outlined by Maas, E. and Hoffman, G. (1977), who described crop salt tolerance as a linear function of the yield reduction with increasing soil salinity. Most plants can exclude Na^+ and Cl^- effectively via roots while water is absorbed from the soil (Munns 2005). Halophytes have the ability to maintain this exclusion at higher salinities than glycophytes. For example, sea barley grass, *Hordeum marinum*, can exclude Na^+ and Cl^- up to least 450 mM NaCl (Garthwaite et al. 2005). In arid and semiarid lands, plant water uptake may suffer from drought as well as the low soil water potential caused by salinity. Therefore, these plants have evolved mechanisms to tolerate the effect of water stress.

Many factors influence salt tolerance, including plant type and stage of plant growth. For example, rice (*Oryza sativa*) is considered a salt sensitive crop while barley (*Hordeum vulgare*) is considered a tolerant crop (Figure 2-5). Bread wheat (*Triticum aestivum*) has a moderate tolerance. Therefore, understanding the mechanism of salinity stress in crops is very important to minimising the effect on crop production.

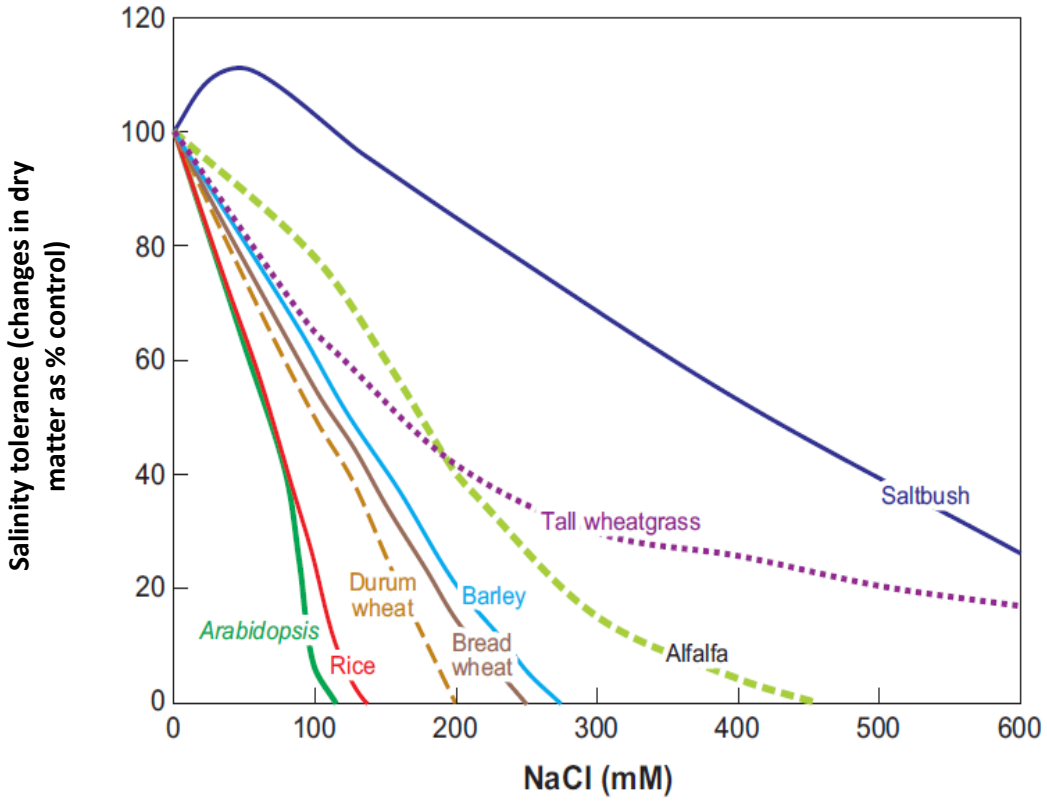

Figure 2-2: Salt tolerance of different crops (Munns & Tester 2008)

Effects of salinity stress on plant growth

Irrigation with saline-sodic water leads to the risk of salt accumulation in the root zone reducing plant growth and yield due to the reduction of soil water potential causing osmotic stress and leading to ion specific toxicities (Asgari et al. 2012; Chinnusamy et al. 2005). Munns and Tester (2008) note that both sodium (Na^+) and chloride (Cl^-) may be responsible for osmotic and toxic effects, which lead to a significant reduction in crop growth. In addition, irrigation with saline-sodic water may also affect the soil physical properties (i.e. soil structure) with a resultant impact on plant growth by influencing root distribution and the efficiency to take up water and nutrients (Blum & Rampazzo 1993).

a. Osmotic stress

The effect of osmotic stress is similar to the stress caused by drought. Plants under saline stress use energy required for other physiological processes to extract water from the soil (Katerji et al. 2003). While crops can tolerate low salt concentrations in the root zone, a concentration in the soil solution that exceeds the crop threshold impacts on plant growth and yield (Maas, E. & Hoffman, G. 1977). The reduction in crop water uptake reduces the movement of water and ions towards the root surface. This may also reduce the rate of nutrient movement towards the root and impact on nutrient uptake. Thus, osmotic stress impacts negatively on plant growth rate and water and nutrient uptake (Munns & Tester 2008).

b. Specific Ion Effect

Specific elements (including sodium and chloride) are essential to plants in very low amounts but can cause toxicities at high concentrations (Ayers & Westcot 1985). Generally, increasing concentrations of salt in soil solution may lead to nutritional disorders impacting directly on plant growth (Quist & Williams 1999). High levels of Na^+ may lead to a decrease in plant uptake of K^+ (Greenway & Munns 1980). In many species, a higher concentration of K^+ in growing tissues is related to salt tolerance. In addition, boron can cause toxicity to sensitive crops at concentrations less than 1 part per million (ppm) (Bauder et al. 2011).

2.5 Traditional management of irrigation with saline-sodic water

The application of saline–sodic irrigation water is a major reason for soil salinisation, sodification and nutrient loss in irrigated areas. The application of soil amendment or use of water treatment is used to reduce the effects on soil irrigated with saline-sodic water. Blending or alternating saline-sodic water with good quality water is also used. However, the application of additional water (i.e. leaching fraction) is most commonly need to minimise salts in the root zone. In this method, greater amounts of irrigation water are applied to leach salts from the root zone in order to maintain the concentration of salts under the threshold salinity, while in the close system this method cannot be used due to the accumulation of salt will be occurred (no draining water). According to equation (2-5), the root zone salinity (EC_{se}) can be calculated from the irrigation water salinity (EC_i) and the root zone leaching fraction (LF), as listed in Table 2-2 for four broad soil types (ANZECC 2000).

$$\mathbf{EC_{se}} = \frac{EC_i}{2.2 \times LF} \qquad \textbf{Equation 2-5}$$

where:
EC_{se} = average root zone salinity in dS/m
EC_i = electrical conductivity of irrigation water in dS/m
LF = average leaching fraction.

However, the addition of excess water to leach salts may lead to the leaching of nitrogen and other mobile ions beyond the root zone, adversely affecting groundwater quality and crop production.

Table 2-2: Soil type and average root zone leaching fraction (ANZECC 2000) from (DNR 1997a)

Soil type	Average root zone LF
Sand	0.6
Loam	0.33
Light clay	0.33
Heavy clay	0.2

2.6 Application of electric field to soils

Electro-kinesis (EK) is the process of applying an electrical field to transport a solute through a porous medium. The application of an electric field to transport water and ions through capillary pores was first used by Reuss c.a. 1809 (Mitchell & Soga 2005).

This researcher found that water moved through capillary pores towards the cathode when an electric field was applied to a clay water mixture. When the electric potential was removed, the water stopped moving (Mitchell & Soga 2005). Applying an electrical current (in the range of mA cm^{-2}) generates physical, chemical and hydrological changes in the soil (Acar et al. 1995). The main phenomena includes electrolysis and the transport processes electro-osmosis, electro-migration (ionic migration), and diffusion (Acar & Alshawabkeh 1993; Reddy & Cameselle 2009). Figure 2-3 shows a simplified description of the EK transport processes.

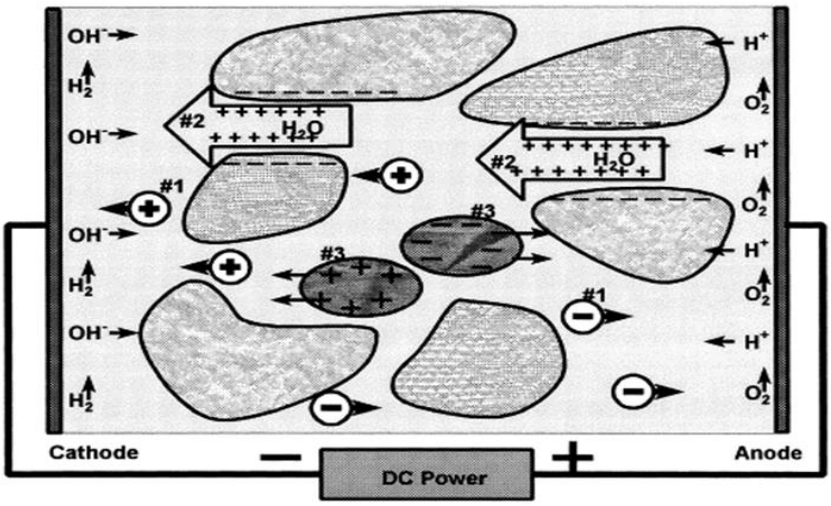

Figure 2-3: The processes occurring in electrokinetic remediation (Leinz et al. 1998)

2.6.1 Electrolysis

Electrolysis is the cause of oxidation and reduction processes at the electrodes. Applying an electrical current through electrodes causes a loss or gain of electrons by ions in the solution (Bockris & Reddy 1970). Consequently, ions which lose electrons become positively charged (cations); whereas ions which gain electrons will be negatively charged (anions). The removal of electrons is oxidation, occurring at the anode (positive charged electrode); while the gain of electrons is reduction, occurring at the cathode (negative charged electrode) (Bockris & Reddy 1970).

Electrolysis of water is the primary reaction at the electrodes when applying an electrical field to a soil (Gray 1900; Mise 1961; Reddy & Cameselle 2009). As a result of this reaction, hydrogen gas will be generated at the negative electrode (anode); while oxygen gas will be produced at the positive electrode (cathode) (Zoulias et al. 2004). These reactions (equations 2-6 and 2-7) affect soil pH as the pH of the pore fluid will be acidic (pH <4) at the anode and basic (pH >10) at the cathode.

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+$$ **at anode (oxidation)** **Equation 2-6**

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$ **at cathode (reduction)** **Equation 2-7**

2.6.2 Electro-osmosis

Electro-osmosis (EO) occurs due to the electric gradient and it is responsible for the solution movement which contains dissolved ionic and non-ionic species toward the electrode (Acar et al. 1995; Reddy & Cameselle 2009). This phenomenon appears with the application of electrical potential through electrodes on the soil column which creates the movement of water molecules from the anode to the cathode due to the different electrical potential between the negatively charged soil surface and the soil

solution (Casagrande 1900; Das 2013). Thus, electro-osmosis can be defined as the consequences of the different electrical charges in the soil capillary, or pore wall, and the adjacent pore water because the pore wall attracts the positively charged water molecules present in the pore space (Leinz et al. 1998).

The earliest observation of electro-osmosis flow was reported by Reuss in 1808 (Paillat et al. 2000). Wet fine-grained (clay soil) included two charged layers (negative and positive charged layers). The clay surface of the capillary wall is negatively charged and attracts a layer from the soil solution. By applying an electric current via electrodes placed in the soil the positive charged ions will attract to the cathode and move water in the same direction (Mitchell 1993). Equation 2-8, which is analogue to Darcy's law, describes the EO-induced water flow rate for applied purposes (Alshawabkeh et al. 1999; Bjerrum et al. 1967).

$$Q_e = K_e E A \qquad \textbf{Equation 2-8}$$

Where Q_e indicates the EO-induced water flow rate (m^3s^{-1}); K_e = the coefficient of electro-osmotic conductivity ($m^2V^{-1}s^{-1}$); E = the electric field strength ($V\ m^{-1}$) and; A = total cross-sectional area perpendicular to the direction of fluid flow (m^2).

The coefficient of electro-osmosis, as described in equation (2-8), is directly related to the Zeta potential of the soil-pore fluid interface ζ (V), the soil electrical permittivity ε ($C^2N^{-1}m^{-2}$) and soil porosity n (unit less). However, it is inversely proportional to the viscosity of the pore fluid η ($N\ s\ m^{-2}$) and 4π which is a shape factor describing the spherical shape of particles (Acar & Alshawabkeh 1993; Arnold 1973; Banerjee & Law 1998). The K_e value depends on the soil type which generally is between 1.5 x 10^{-9} and 12 x 10^{-9} $m^2\ V^{-1}\ s^{-1}$ (Mitchell & Soga 2005);

$$K_e = \frac{\varepsilon \zeta}{4\pi\eta} n \qquad \textbf{Equation 2-9}$$

In the EO process, the water flow occurs as a result of both the applied electrical gradient and the hydraulic gradient. The hydraulic flow (q_h) due to the hydraulic gradient (i_h) is described by Darcy's law (Reddy & Cameselle 2009).

$$q_h = k_h i_h , \qquad \textbf{Equation 2-10}$$

where (k_h) is the hydraulic conductivity.

2.6.3 Electro-migration

Electro-migration (ionic migration) is the movement of dissolved ionic species. The anions migrate towards the anode while cations move towards the cathode at the rate dependent on the ionic species mobility (Reddy & Cameselle 2009). Figure 2-4 shows a simplified description of the ions movement in soil under electro-migration.

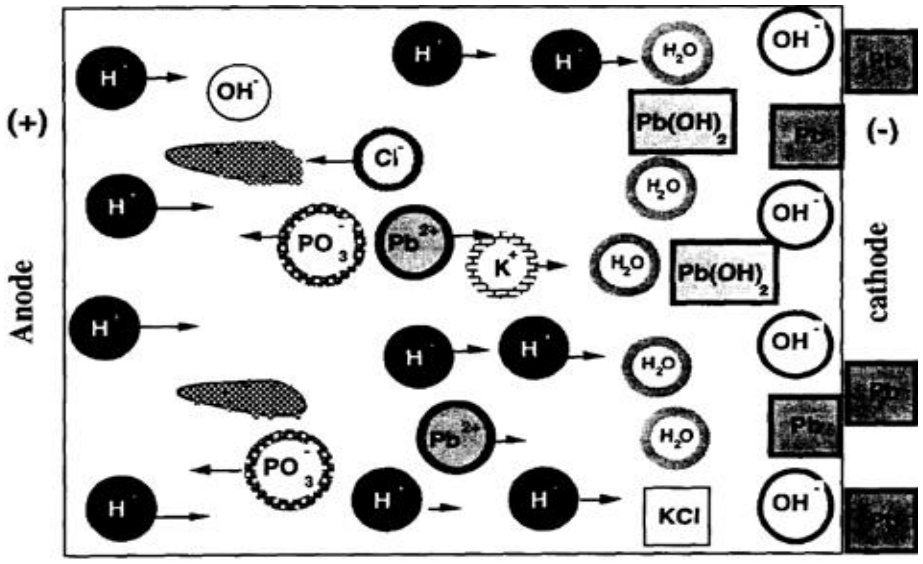

Figure 2-4 : The migration of ions across the soil to opposed charged electrode under an electric field (Acar et al. 1995).

The migration of ions toward electrodes occurs when an electrical field is applied. However, the amount of ionic migration is affected by the ionic mobility. The values of ionic mobility in dilute solutions vary among ions. The typical range of these values is 3×10^{-8} to 1×10^{-7} m^2 $V^{-1}.s^{-1}$, 'except for H^+ and OH^-, which have mobilities one order of magnitude greater' (Baraud et al. 1997; Page & Page 2002). The mass transport of ions by migration can be calculated by using equation 2-11 (Acar & Alshawabkeh 1993).

$$J^m_j = - u^*_j c_j \nabla E \qquad \text{Equation 2-11}$$

where, J^m_j refers to migration flux of salt ions, u^*_j is effective ionic mobility, E = electrical potential.

The effective ionic mobility (u^*_j) is defined as the velocity of the ion in soil pores under effect of a unit electric field (Alshawabkeh & Acar 1996). It can be theoretical estimated by using the Nernst-Townsend-Einstein relation (Holmes & Handler 1962).

$$u^*_j = u_j\ \tau n = \frac{D^*_j}{RT} z_i F \qquad \text{Equation 2-12}$$

where, u_j = ionic mobility, D^* = the diffusion coefficient (m^2/s) z_j is valence, F = Faraday's constant, R = the universal gas constant and T is absolute temperature

2.6.4 Diffusion

Diffusion can be defined as a process of ions transport occurring in response to a concentration gradient especially near the electrodes (Page & Page 2002). The common law describing the flux of ions in solution affected by diffusion is Fick's law (Acar & Alshawabkeh 1993):

$$J_d = D^* \nabla (- C_i) \qquad \text{Equation 2-13}$$

where, J_d = the flux of ions due to diffusion effect ($mol/m^2.s$), D^* is the effective diffusion coefficient (m^2/s) and C_i is molar concentration.

The effective diffusion coefficient of the salt ions in the porous medium (i.e. soil) is related to the diffusion coefficient in free solution which are constrained by the soil porosity and a tortuosity factors.

$$D^* = D_i \tau n \qquad \text{Equation 2-14}$$

where, τ is tortuosity factor, D_i is diffusion coefficient in free solution at infinite dilution ($cm^2 s^{-1}$).

2.6.5 Electrophoresis

Electrophoresis is defined as the transport of charged particulates when an electric field is applied (Acar & Alshawabkeh 1993; Mitchell & Soga 1976). Applying an electric field in a soil-water system leads to the negative charged particulates moving to the anode while the positive charged particulates move toward the cathode. Electrophoresis can be important in transporting dispersed clay particulates in soils (Acar & Alshawabkeh 1993; Paillat et al. 2000).

2.6.6 Other effects associated with applying an electric field in soil

Application of an electric field through a soil may also have an impact on temperature. This occurs when the high electric field is applied. For example, Shang and Dunlap (1996) reported that extreme heating of the soil was noticed after applying 200 V m^{-1}. Furthermore, Casagrande (1949) observed that heating and energy losses occurred when a voltage gradient greater than 50 V m^{-1} was applied.

2.7 Applications of electro-kinesis in soil

EK processes have been used to remove salts and contaminates from subsurface drains or soils. Figure (2-5) shows a typical field electro-kinesis remediation system.

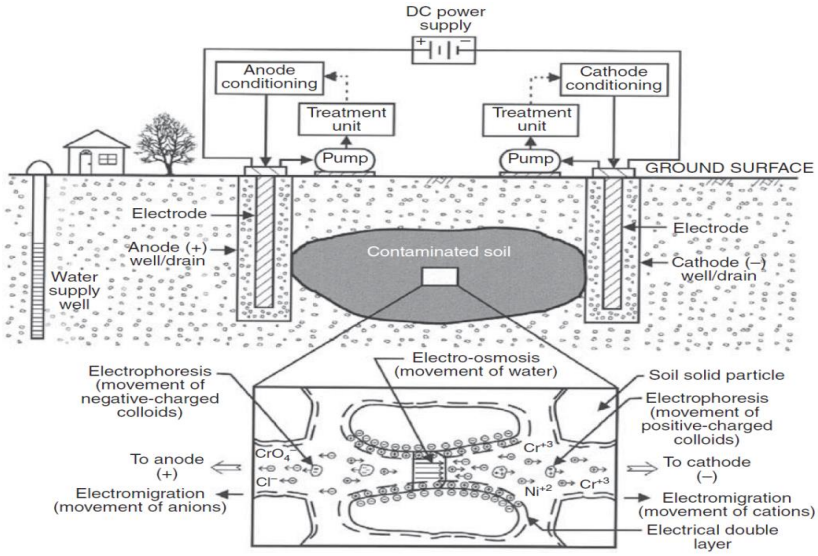

Figure 2-5: Concept sketch describing the application of EK as a remediation system in a contaminated site (Reddy & Cameselle 2009).

Many studies have tested applications of EK to remove and control different species. For example, Acar et al. (1994) studied the removal of cadmium (Cd) II from saturated kaolinite by application of EK and found that approximately 90-95 % of Cd (II) was removed from the Kaolinite. Bruell et al. (1992) examined the application of EK for the removal of hydrocarbons from clay. The results of this study showed that chemicals that have comparatively high solubility and low distribution coefficients such as

benzene, toluene, trichloroethylene (TCE), and m-xylene were easily detached from kaolin by EO; however, chemicals that have a low solubility and high distribution coefficient, such as hexane and isooctane, were transported from the clay at a slower rate. In addition, Kim et al. (2001) examined the efficiency of using EK to remove lead (Pb) and cadmium (Cd) from the soil. This study reported that approximately 75-85% of Pb and Cd were removed efficiently from kaolinite soil and 50-70% was removed from a tailing soil over a period of more than 4 days.

Jeon et al. (2015) tested the ability of an in situ EK process to remove As, Cu and Pb from a contaminated paddy rice field soil. It was observed that approximately 44.4 % of the As, 40.3 % of the Cu and 46.6 % of the Pb were removed from the soil after 24 weeks of applying the electrical field. According to El-Sawaby and Vadyunina (1977), the application of EK to saline soils led to an increase in the salt content of the drainage water when compared to leaching with water alone, but these differences decreased over time.

Electro-osmosis has been used in different ways including soil contamination treatment, dewatering biomass and the dewatering process of sludge (Al-Asheh et al. 2004; Bjerrum et al. 1967; Lockhart 1983; Mohamedelhassan & Shang 2001; Xue et al. 2015).

Electro-osmosis has been used as a dewatering technique. Water can be simply removed from a material after placing this material between electrodes and applying electrical potential. Following the classic investigations of Station and Casagrande (1947) on the capability of applying electric field for dewatering of clay soils, several researchers used electro-osmosis for dewatering (Adamson et al. 1966; Bjerrum et al. 1967; Casagrande 1949; Fourie et al. 2007; Shang & Lo 1997).

Shapiro and Probstein (1993) removed 94% of effluent contaminates from saturated clay using a direct current electro-osmotic dewatering technique. Reddy et al. (2006) investigated the feasibility of using electro-osmosis for de-watering of sediment. Applying the electric potential reduced the initial moisture content by 35% and 51%, respectively near the bottom and at the top of the sediment sample, compared to less than 5% moisture content reduction by gravity alone. Furthermore, Zhou et al. (2001) dewatered sludge and found that applying an electrical field of 1200 V/m removed 60% of the water while 35% removal was achieved at 400 V/m and gravity alone removed less than 20%.

The use of electro-kinesis as a remediation method for specific ions has been evaluated by several researchers. For example, Cho et al. (2009) used an electrical field to remove salt from a soil and found that approximately 82% of nitrate was removed; while less than 50% of chloride and sulphate ions were removed. These results support that the ion removal efficiency depends on the specific ion mobility. Kim et al. (2001) examined the efficiency of using electro-kinetic to remove lead (Pb) and cadmium (Cd) from soil. This study reported that approximately 75-85% of Pb and Cd was removed from a kaolinite soil and 50-70% was removed from a tailing soil over a period more of than 4 days. In laboratory scale with brick, Ottosen and Rörig-Dalgård (2007) investigated the ability of electro-migration to remove $Ca(NO_3)_2$. They found that the nitrate and calcium concentrations could be effectively reduced by electro-migration.

2.8 Nitrate maintenance by electro-kinesis

Cairo et al. (1996) evaluated EK using subsurface horizontal drainage tubing and parallel electrodes to collect and extract nitrates from soil. These authors found that the application of a small direct-current electrical field to the soil resulted in an increase in the nitrate concentration at the anode and a decrease in concentration at the cathode demonstrating the movement of the nitrate from the cathode to the anode. Eid et al. (2000) also tested the nitrate gradient developed in response to an electrical potential. This laboratory experiment tested two systems; a closed system (no flow) and an open system with flow opposite to the direction of the electric current. This study showed that the application of EK effectively concentrated and maintained the nitrate near to the anode although the pH gradient affected the movement of NO_3 via the soil column. Moreover, Jia et al. (2006) evaluated the application of electro-kinesis on nitrate movement in wet soil. This study showed that nitrate concentration increased at the anode while sodium and calcium concentration were reduced; also reported a lower pH value near the anode. Recently, García et al. (2015) evaluated EK to remove nitrate from a clay soil and found that application of an electrical field removed about 90% of the nitrates from the soil in less than a week.

2.9 Conclusions and implications for managing EK with irrigation

The ability to use EK to remove salts from a soil and maintain nitrates near the anode has been demonstrated in sections 2.7 and 2.8. However, to use EK in agricultural applications it needs to be managed to maintain root zone factors suitable for plant growth and yield. Maximising plant growth and yield requires optimal management of soil water, nutrients, pH and EC. EK has the ability to influence each of these factors in the root zone but has not been evaluated for irrigated conditions.

The effects of the EK processes on soil pH have been discussed in the previous sections. It was shown that the lowest pH occurs at the anode while the highest value occurs at the cathode. These changes have direct and indirect impacts on plants due to effects on the solubility and availability of nutrients. Therefore, maintaining pH at moderate values is an important challenge when using EK as a management tool in agriculture.

The excessive application of irrigation water to leach salts from the root zone leads to the loss of nutrients via drainage water. Therefore, selecting the application irrigation method and practices to avoid these issues is important to successful management.

Traditionally, greater amounts of irrigation water are applied to leach salts from the root zone in order to maintain the root zone concentration of salts under the threshold for plant damage. However, the addition of excess water for leaching of salts may lead to leaching of nitrogen beyond the root zone, degrading groundwater quality and reducing crop production. To address these issues, the electro-kinesis technique has been tested and evaluated as alternative management method.

Section 2.7 discussed several studies that have evaluated the use of EK as a chemical remediation method. This technique has been shown to effectively remove heavy metals and contaminants from affected sites. Section 2.8 demonstrated that nitrates can be concentrated near the anode due to electro-migration. However, while previous studies have shown that EK may be useful as a management method to manage salts and to maintain nitrate in the root zone when irrigating with saline water, little research has been conducted to evaluate the practical operation of EK under irrigation

conditions. Therefore, this research will evaluate the potential use of EK to improve management of irrigation with saline water by reducing salt accumulation in, and nitrate loss from, the root zone.

Chapter 3: General Methodology

3.1 Introduction

Laboratory experiments were conducted in order to evaluate the potential to use electro-kinesis (EK) to improve the management of soils irrigated with saline-sodic water. Preliminary experiments were conducted to investigate the effect of EK on salt drainage (Chapter 4) and nitrate movement (Chapter 5) in sand columns. This was followed by a study investigating the ability to simultaneously improve the management of nitrate retention and salt drainage using EK in a sand irrigated with saline-sodic water (Chapter 6). This led to the development of a combined soil-water and EK model (Chapter 7) which was used to demonstrate the effect of management variables on the ability to improve nitrate and salt management. As many of the materials and methods used in these experiments were similar, this chapter describes the common components. Details specific to each experiment are described in the relevant chapters.

3.2 Soil and column preparation

A local river sand was sourced from a commercial landscape supplier. The sand was washed with distilled water then dried in an oven at 105ºC for 48 hours before being passed through a 2 mm screen sieve and thoroughly mixed. The sand (Table 3-1) was then stored in air-tight plastic containers until use.

Table 3-1: Selected properties of the washed sand

Properties	Unit	Value
EC (1:5 soil-water ratio)	dS m^{-1}	0.04 ± 0.02
pH (1:5 soil-water ratio)		6.6 ± 0.01
Clay	%	0.0
Silt	%	0.0
Sand	%	100

Columns of the sand soil were prepared using sections of PVC pipe (internal diameter = 10 cm; length = 10 cm). The sand was progressively poured into a single section of PVC pipe (with bottom fitted with a fine plastic wire mesh and covered with a Whatman 42 filter paper), spray misted and mixed with a water solution (constituents and concentration dependent on the experiment) to produce a specified water content, and packed to a bulk density (ρ_b) of 1.5 ± 0.05 g cm^{-3} using a flat headed tamping rod.

To ensure that the packed soil density was consistent throughout the sand column, approximately ½ of the total soil volume required to fill the PVC section was added at a time and then tamped. This was repeated so that two volumes of soil were successively added and tamped before the pipe section was fully packed. A second PVC pipe section (without the bottom mesh and filter paper) was then attached to the top of the first section and a watertight seal between the pipe sections created using PVC tape. Soil was then added into the second section of pipe in a similar manner to the first section and soil packing continued. Additional pipe sections were added and soil packing continued until the full sand column length (30 or 50 cm) was reached.

Flexible 1 mm thick, carbon fibre material (Carbon Fiber Australia, Warragul) was used to construct both the cathode and anode (5 cm wide). The anode and cathodes

were installed as a ring around the inside surface (circumference) of the PVC pipe prior to soil packing (see Figure 3-1). The anode was installed 2.5-7.5 cm from the top surface of the sand column while the cathode sheet was installed 2.5-7.5 cm from the bottom surface of the sand column with both electrodes having wire connectors fitted through the side of the PVC pipe.

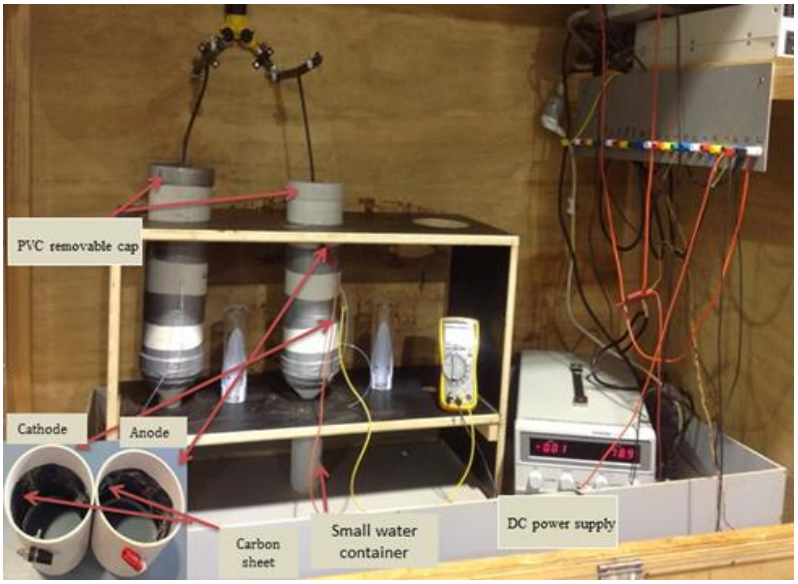

Figure 3-1: Sand columns mounted in wooden frame and attached to the EK equipment within the electrically isolated wooden cupboard. Insert shows electrodes mounted inside PVC piping

Solution extraction tubes (1 mm diameter × 13 cm length) were installed horizontally (laid in circle with diameter = 4 cm) into the centre of the sand columns at specified depths (generally 5, 15, 25, 35 and 45 cm) during soil packing. The tubes were mounted through a small hole located in the middle of each PVC section, assuming the solution draw from the tubes at 5, 15, 25, 35 and 45 cm depth would be a sample of the liquid phase in the depths of 0-10, 10-20, 20-30, 30-40 and 40-50cm, respectively, and enabled extraction of solution during the experiment. A vacuum was applied to the extraction tubes by attaching a 50 ml plastic syringe and fully extending the plunger (Figure 3-2) and held in place using a plastic block (Figure 3-2) for a period of >1 hour.

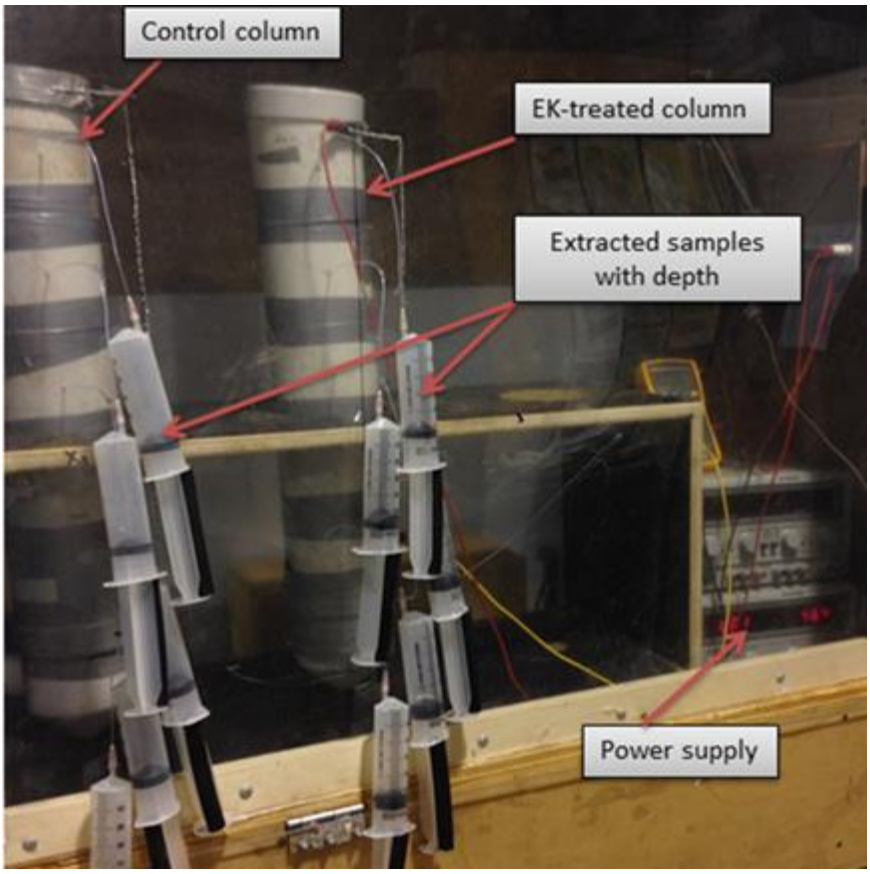

Figure 3-2: The application of the vacuum to the porous soil solution extraction tubes by extending the syringe plungers and holding the plungers in place with black plastic blocks

After soil packing, the column base was inserted into a plastic Buchner funnel and the join between the column and funnel sealed with PVC tape. The sand column was then mounted vertically in a wooden frame (see Figure 3-1) and the top surface fitted with a removable PVC cap in which a small hole had been drilled to enable the application of drip irrigation while minimising evaporative losses.

3.3 Preparation of the salt solutions and application of water to the sand columns

Saline-sodic salt solutions were prepared and applied to the sand columns both during soil packing (section 3.2) and by irrigation during experimentation. Combinations of calcium chloride ($CaCl_2.2H_2O$) and sodium chloride (NaCl) were dissolved in distilled water to prepare a range of saline-sodic water qualities with different electrical conductivity (EC) and sodium adsorption ratio (SAR). After preparation, the EC of the solution was confirmed by measuring three sub-samples using a calibrated EC meter (LabCHEM- CP-Cond/pH, version 1.01).

The irrigation waters were applied to the sand columns using a drip irrigation system (Figure 3-3). The irrigation system consisted of a plastic container (15 L) placed above the columns to provide a >0.5 m of head pressure. A plastic tube was connected to the water tank and the other end of the tube was split into two tubes to enable separate irrigation of two columns. The amount of water added to the columns was then

controlled by valves connected with a dripper at the top of the columns. The columns were allowed to free drain.

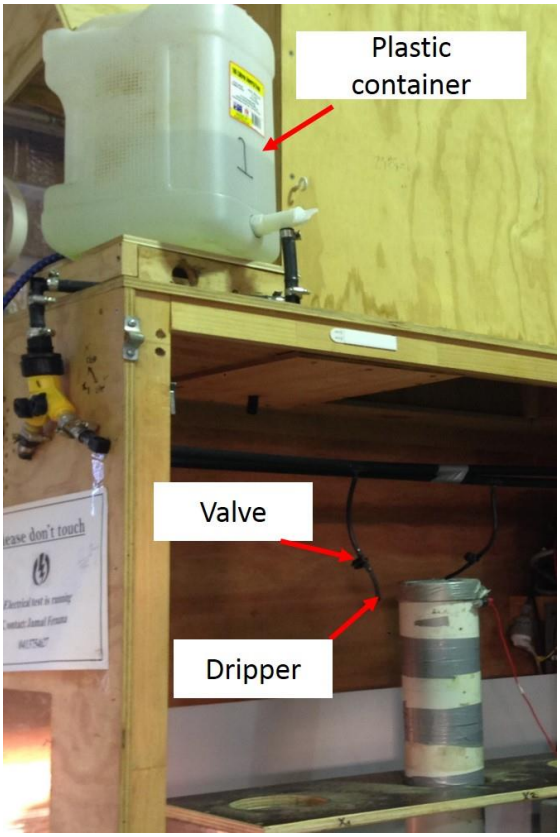

Figure 3-3: Configuration of the irrigation system apparatus

3.4 Application of the electro-kinetic field

The wooden frame holding the sand columns and the majority of the monitoring and electrical power generating equipment were installed within an electrically isolated wooden safety cupboard fitted with isolation switches (Figures 3-1 and 3-2). The cupboard was also fitted with a clear perspex front wall to enable visual observation of the columns and power supply during experimentation. A DC power supply (GPR-11H30D-1.2 DC 330 watts) which was able to be used in either constant current or constant voltage mode applied the electrical field to the sand columns. The electrical power was generally applied as a constant current at ≤ 1.1 A and ≤ 110 V.

3.5 Measurements and chemical analyses

Measurements of the electrical voltage being applied when a constant current was used were recorded from the power supply digital screen at regular intervals. Soil solution samples were also extracted from the sand columns at times which varied according to the experimental needs. Where appropriate, both the total drainage and rate of drainage were recorded during the experiment at suitable intervals.

Soil samples were commonly taken post-treatment from different depths within the sand column. These were used to measure gravimetric water content using the method of Hesse (1971) and soluble ions following the method suggested by Rayment and Higginson (1992).

To determine gravimetric water content, ~10 g of sampled soil was weighed using an electronic scale (OHAUS corporation, USA, d = 0.1 mg) and then dried in an oven at 105 C° for 24 hours. The soil sample was then taken out of the oven and allowed to cool for 30 minutes in a desiccator prior to re-weighing and the gravimetric water content calculated using:

$$\textbf{\textit{Gravimetric water content}}\ (\%) = \frac{\textit{Soil wet weight} - \textit{soil dry weight}}{\textit{soil dry weight}} \times \mathbf{100} \qquad \textbf{Equation 3-4}$$

For the measurement of soluble ions, ~5 g of air dried soil was weighed in an aluminium container of known weight, transferred to a centrifuge tube (45 cm^3) with 25 cm^3 of distilled water and mixed by a shaker (John Morris Pty. Ltd, Model No 3521, Illinois USA) for 10 minutes at 100 rpm. The tubes were then placed in centrifuge (Labtek Pty. Ltd, Model No, 650.550.050, Australia) for 15 minutes at 3000 rpm and the supernatant transferred to a 100 cm^3 container.

A calibrated EC and pH meter (LabCHEM-CP-Cond/pH probe version 1.01, TPS Pty Ltd, Brisbane) was used to measure conductivity and pH temperature compensated to 25ºC. Where appropriate, supernatant solution samples were diluted prior to analysis for sodium, chloride and nitrate. Soluble sodium (Na) was measured using a SHIMADZU Atomic Absorption Spectrophotometer (AA-7000 connected with auto-sampler) while soluble nitrate Cl^- and NO_3^- was measured by using a DIONEX Ion Chromatography System (ICS-2000), where the flow rate was 1 mL min^{-1} and the run time was 18 min per sample.

Chapter 4: A preliminary evaluation of using electro-kinesis to control salt movement in an irrigated sand column

4.1 Introduction

Worldwide there is increasing demand for food and the shortage of good quality irrigation water has led to the use of alternate sources of irrigation water, particularly in arid and semi-arid areas. In particular, marginal water such as saline-sodic groundwater and industrial effluent water are increasingly used for irrigation (Fereres & Soriano 2007; Pereira et al. 2002). Long-term use of saline-sodic water may have negative impacts on soil productivity due to salinisation and sodification. This can affect soil structure (Aylmore 1993; Tedeschi & Dell'Aquila 2005) and potentially decrease plant water uptake due to reduced water holding capacity and an osmotic effect (Ayers & Westcot 1985; Brinck & Frost 2009). Research (Bauder & Brock 2001; Bennett & Raine 2012b; Chi et al. 2012; Ezlit et al. 2013) has shown that the impacts of irrigation with saline-sodic water can be reduced by improvements in land and water management.

Traditional irrigation management of saline-sodic soils (Chapter 2.5) includes the application of chemical amendments and additional water to leach salt from the root zone (Abbott & McKenzie 1986; Bauder & Brock 2001; Choudhary et al. 2011). Common amendments include gypsum ($CaSO_4 \cdot 2H_2O$), lime ($CaCO_3$) and organic matter (Bennett, J. et al. 2015; Bennett, J. M. et al. 2015; Bennett et al. 2014; Qadir et al. 2001). However, the effectiveness of these amendments in removing sodium from a root zone is soil specific and gradual, dependent on cation exchange (i.e. sodium for calcium) and subsequent leaching of the sodium from the root zone (Bennett, J. et al. 2015; Bennett et al. 2014; Valzano et al. 2001). Conversely, excessive water added to leach sodium and salts can increase leaching of nitrogen to groundwater (Li et al. 2007).

Previous studies (Acar et al. 1994; Acar et al. 1995; Alshawabkeh & Acar 1996; Alshawabkeh et al. 1999; Bruell et al. 1992; Méndez et al. 2011) have shown that electro-kinesis (EK) can be used to remove salts and/or contaminates from a soil. Hence, this technique may be useful in increasing salt drainage from root zones with a reduced requirement for water movement out of the root zone. For example, El-Sawaby and Vadyunina (1977) reported that EK applied to a saline soil led to an increase in the salt content of the drainage water when compared to leaching with water alone. Therefore, the hypothesis of this experiment is that salt in the root zone can be moved, and the salt concentration managed, in an irrigated soil by the application of EK. However, there is little information available on the design and management of EK systems to improve salt management in root zones. Hence, the specific objective of the research reported in this chapter is to understand the effect of electrode separation and electrical current applied on the electro-kinetic movement of salt and changes in pH for an irrigated sand.

4.2 Materials and methods

This trial evaluated the effect of applying EK to irrigated sand columns (30 and 50 cm)' with two different electrode separate distances (20 and 40 cm, where the anode was installed at the top while the cathode sheet was installed at the bottom of the sand column). A control (i.e. no EK applied) and constant current 0.01A treatment for each electrode separation distance were conducted. To evaluate the effect of magnitude of

the electric current applied on salt movement, an additional constant current electrical treatment of 0.02A was applied to 50 cm columns for comparison with the 0.01A 50 cm column treatment (Table 4-1).

Table 4-1: Experimental treatments

Column Length (cm)	Distance between the centre of the electrodes (cm)	Current applied (Amps)
30 cm	20 cm	0
		0.01
50 cm	40 cm	0
		0.01
		0.02

There were two replications of each treatment and hence, a total of 10 sand columns were prepared by packing washed sand into columns of either 30 cm or 50 cm length using the methodology described in section 3.2. Saline-sodic water (EC=4.5 dS m^{-1} and SAR=20) was prepared (as per section 3.3) and added to the sand column during packing to achieve a soil water content equivalent to field capacity (FC).

After sand column preparation, an additional 15 L of the saline-sodic (EC=4.5 dS m^{-1} and SAR=20) (Table 4-2) solution was prepared (as per section 3.3) and transferred to the irrigation tank for application to the columns using the method detailed in section 3.3. The saline-sodic solution was applied by drip irrigation (Section 3.3) at a rate of 60 ml h^{-1} (7.64 mm h^{-1}) for 1 h daily to maintain approximately FC+10% soil moisture during the application of the treatments.

Table 4-2: Irrigation water quality

Water quality	Target		Measured	Mass (mg)	
	SAR	EC (dS m^{-1})	EC (dS m^{-1})	$CaCl_2.2H_2O$	NaCl
Saline-sodic water	20	4.5	4.5 ± 0.01	1050	2210

A constant current of 0.01A was applied continuously for a period of 168 hours (i.e. 7 days) to the 30 and 50 cm EK treatment columns. Following the completion of the 0.01A treatment on the 50 cm columns, a further 0.02A constant current treatment was applied continuously for a further period of 168 hours with daily application of the saline-sodic solution as for the 0.01A treatment. To maintain a constant current application during the treatments, the voltage was automatically varied by the power supply.

Soil solution samples were extracted at different depths (as per section 3.2) from the sand columns every 24 h for 7 days. At the end of the EK application period, soil samples were taken at depths of 5, 10, 15, 20, 25 and 30 cm for the 30 cm columns and depths of 10, 20, 30, 40 and 50 cm for all the 50 cm columns. The leachate was not collected. The soil samples were oven dried at 105˚C for 24 h and the gravimetric water content, electrical conductivity (EC), pH and concentration of sodium and chloride measured using the methods described in section 3.5.

Data are expressed as the mean of two replicate values for each measured parameter. Statistical analyses were undertaken using the Statistical Package for the Social Sciences (SPSS) v19 for Windows 7 (Cramer 2004). Analyses involved univariate ANOVA. Two-Way ANOVA was used to identify the significant differences between treatments. The least significant difference (LSD) was used to compare the means with a probability level of 5%.

4.3 Results

4.3.1 Effect of electrode separation distance

4.3.1.1 *Electrical conductivity (EC)*

Figures 4-1 and 4-2 show a comparison of the sand column initial EC, EC without EK applied (i.e. control), and EC changes due to EK application in the 30 and 50 cm columns, respectively. In general, the application of the saline-sodic irrigation water resulted in an increase in EC during the treatment period while the application of EK resulted in a change in the distribution of the salt (i.e. EC) within the treated sand columns.

The saline-sodic water applications (see the control treatments) generally resulted in a significant (P<0.05) increase in EC throughout the column (Figures 4-1 & 4-2). While the effect was slightly more pronounced in the shallow (i.e. 5 and 15 cm) depths there were generally only small differences in the EC observed at different column depths in the control treatments.

By contrast, the general effect of the EK treatment was to move salt from the bottom towards the top of the columns. Significant increases (P<0.05) in EC were observed at the shallow depths (i.e. 5 and 15 cm) and significant decreases in EC were observed at the bottom depth in both the 30 and 50 cm columns after 24 or 48 hrs of EK treatment (Figures 4-1a,b & 4-2a,b). Increasing the period of EK application generally resulted in a proportionally larger difference in the EC between the top and bottom of the columns. However, as the treatment period increased, the application of saline-sodic water generally resulted in some salt moving down into the bottom column layer (and draining) and hence the EC at this depth typically increased to above the initial EC at longer periods.

Significant differences in the EC were also observed due to the electrode separation distance, particularly after 48 hrs of EK treatment. For example, the EC at 5 cm depth in the 50 cm column increased almost linearly during the EK treatment and was >15 dS m^{-1} after 168 hrs (Figure 4-2h) where as in the 30 cm column, the EC at 5 cm plateaued at ~12 dS m^{-1} after ~96 h of EK (Figure 4-1h). However, the EC in the bottom depth was similar in both the 30 and 50 cm columns after 168 hrs of EK application.

4.3.1.2 *Effect on pH*

The application of EK significantly (P<0.05) affected the soil solution pH throughout sand columns, irrespective of column length (Figures 4-3 and 4-4). The change in pH was rapid in both column sizes with the area near the deeper electrode (i.e. cathode) becoming highly alkaline (pH ~ 12) and the area near the shallow electrode (ie. anode) becoming acidic (pH = 3-4). However, there were significant differences in the rate of change due to electrode separation distance. For example, in the 30 cm column the pH reached an effective equilibrium after ~48 h (Figure 4-3h) but required ~120 h after

EK initiation for equilibrium in the 50 cm columns (Figure 4-4h). In both column lengths, there was a zone of <10 cm over which the soil solution pH transitioned from acidic to alkaline conditions. In both columns, this zone was immediately adjacent to the deeper electrode (i.e. cathode). Hence, the transition zone occurred at a depth of 15 to 25 cm in the 30 cm column but at a depth of 35 to 45 cm in the 50 cm column.

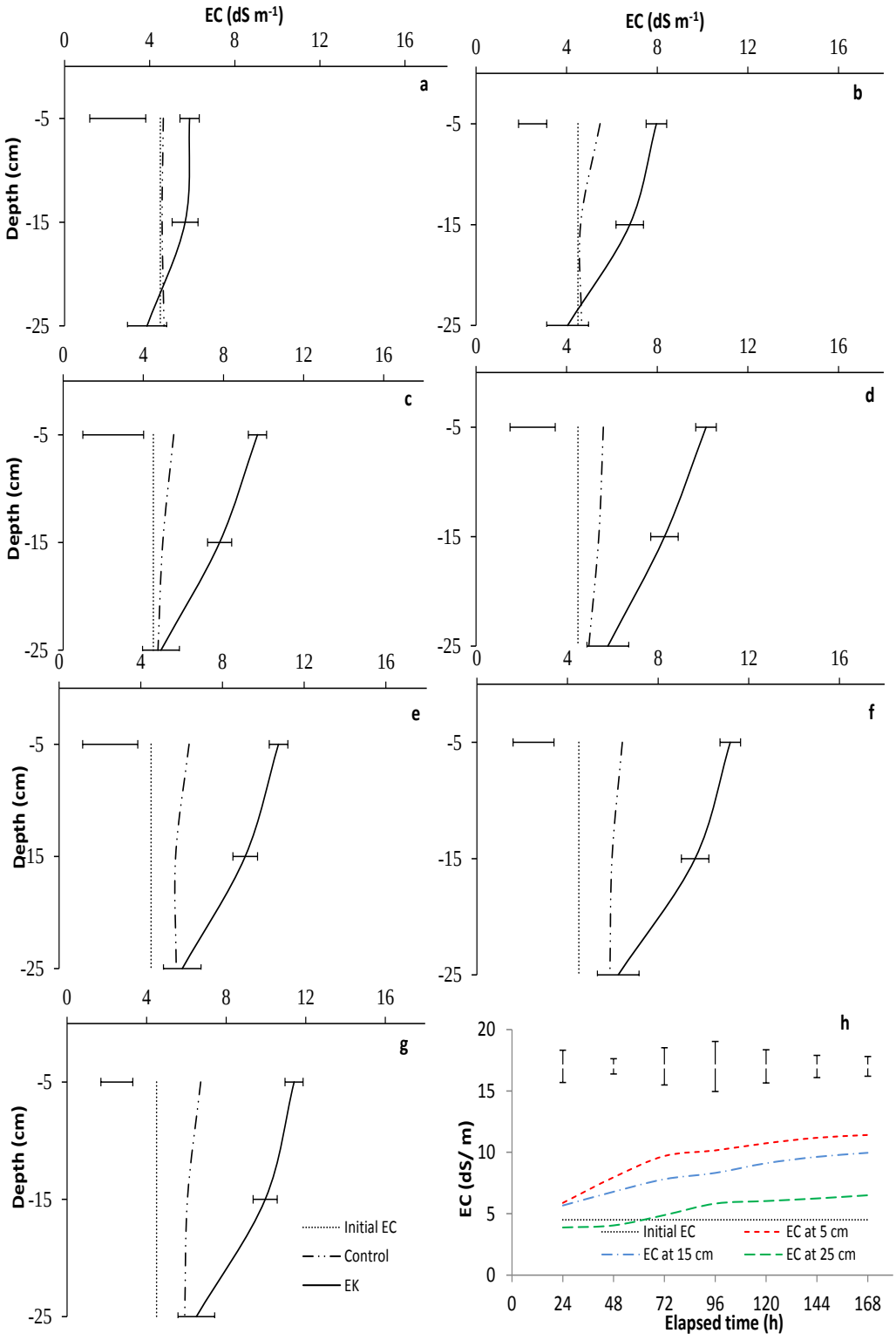

Figure 4-1: Solution EC in 30 cm columns where EK was applied at 0.01 A for (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h, (g) 168 h. Graph (h) shows the effect of EK application time. Horizontal and vertical bars show $LSD_{0.05}$.

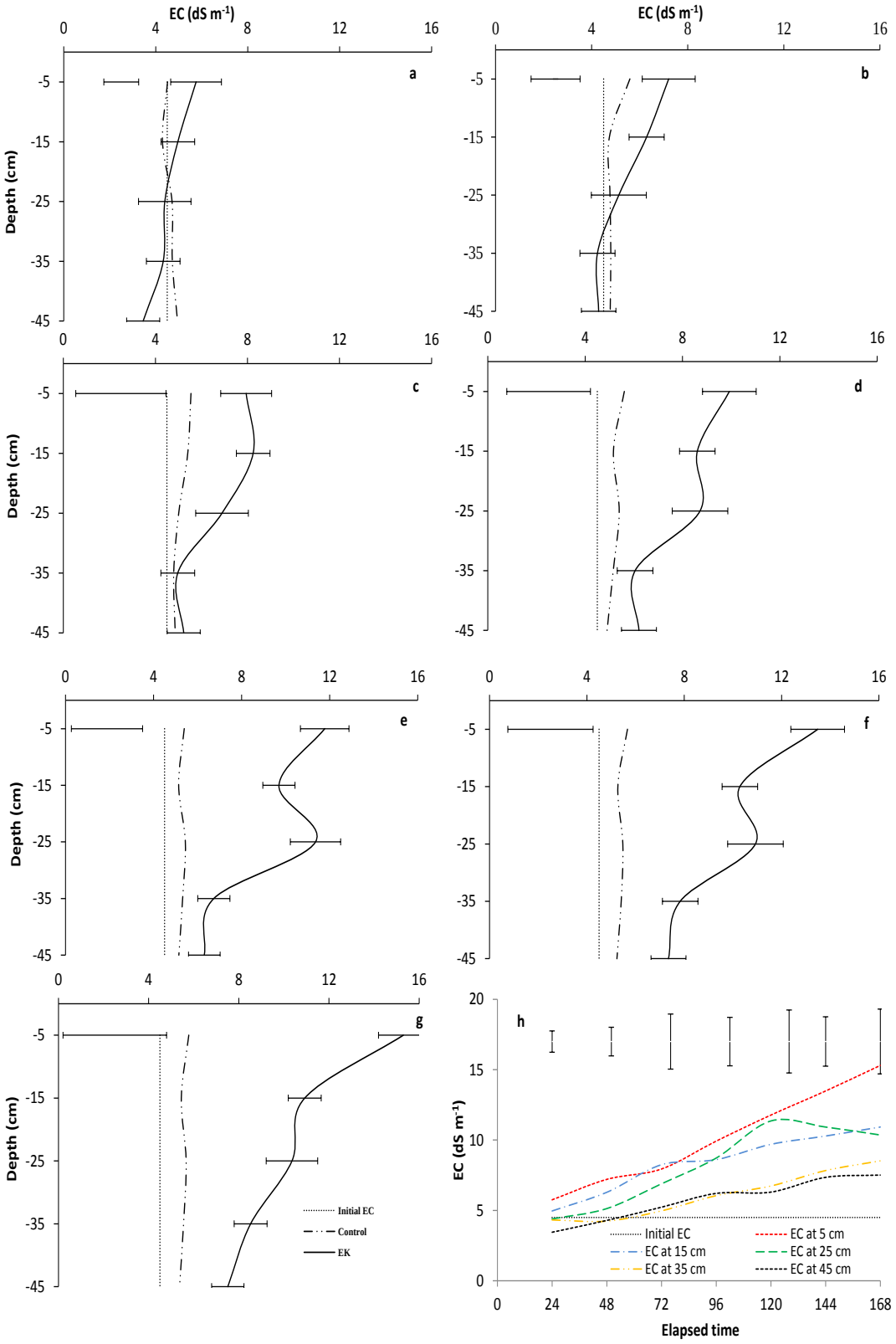

Figure 4-2: Solution EC in 50 cm columns where EK was applied at 0.01 A for (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h, (g) 168 h. Graph (h) shows the effect of EK application time. Horizontal and vertical bars show $LSD_{0.05}$.

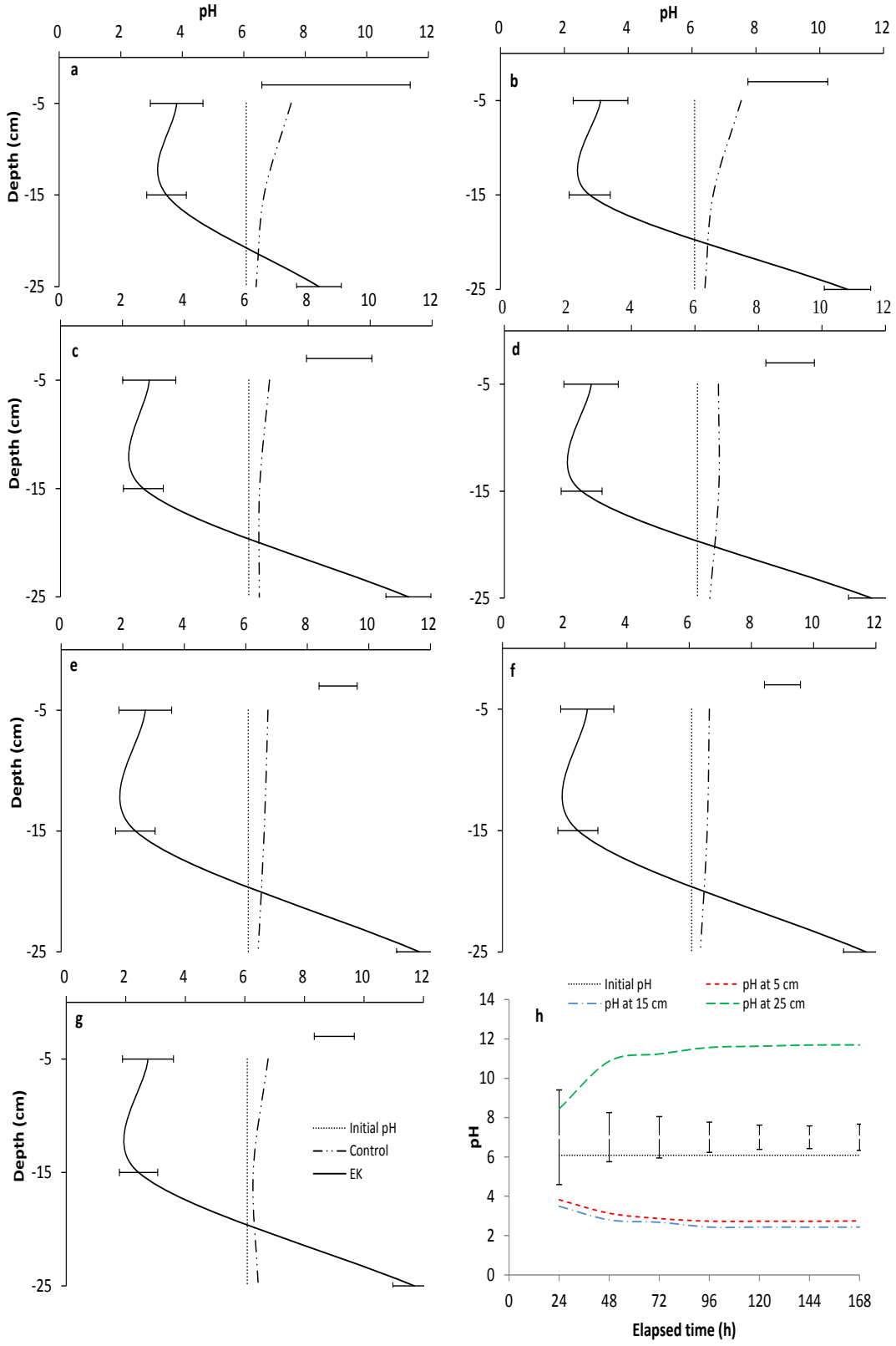

Figure 4-3: Effect of 0.01A EK application on solution pH in a 30 cm column after (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h, (g) 168 h. Graph (h) shows the effect of EK application time. Horizontal and vertical bars show $LSD_{0.05}$.

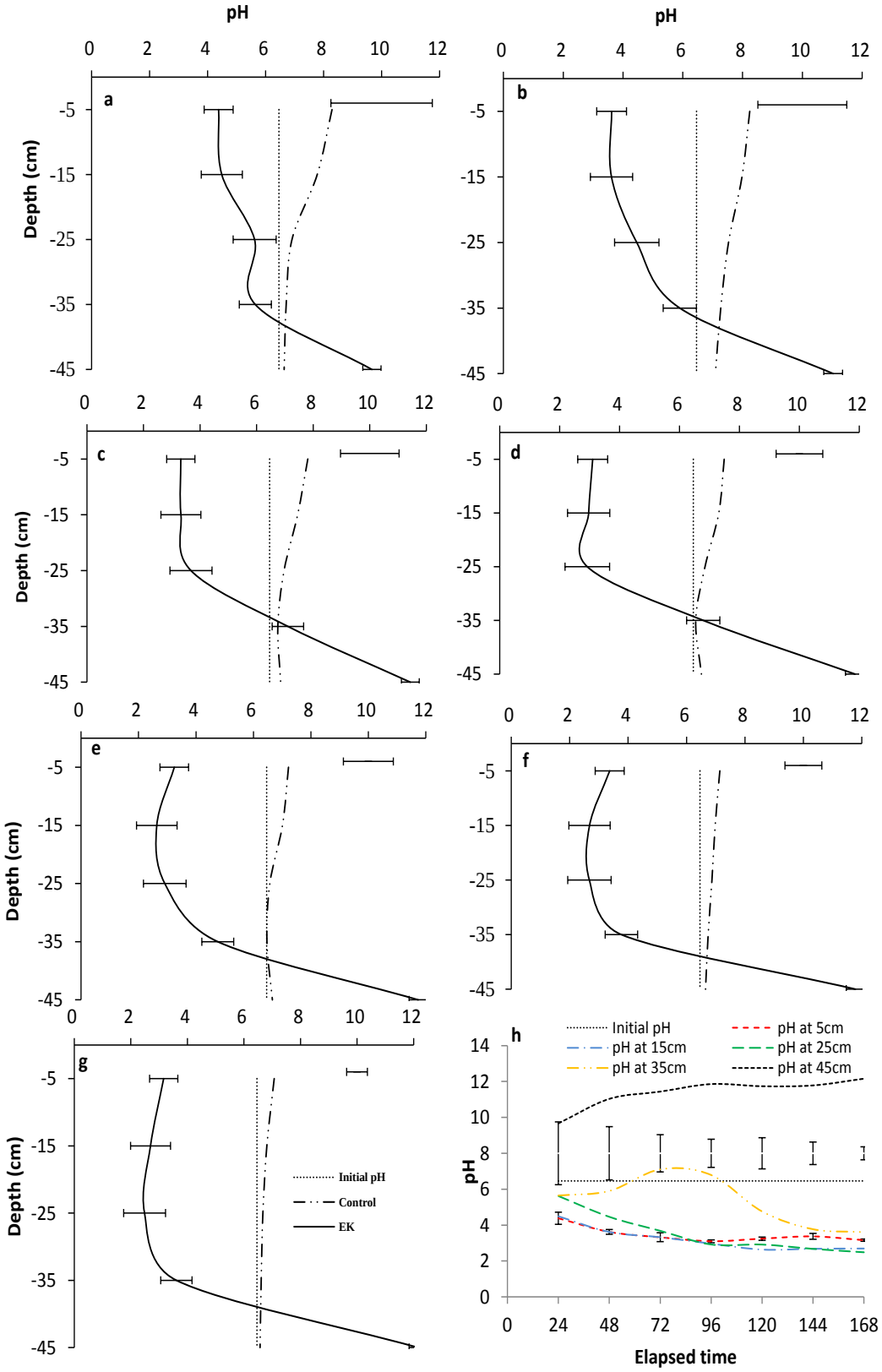

Figure 4-4: Effect of 0.01A EK application on solution pH in a 50 cm column after (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h, (g) 168 h. Graph (h) shows the effect of EK application time. Horizontal and vertical bars show $LSD_{0.05}$.

4.3.1.3 *Effect on sodium and chloride distribution*

The application of saline-sodic irrigation water without EK produced a small but generally significant (P<0.05) increase in sodium concentration which was similar at all depths in the sand columns (Figures 4-5 & 4-6). However, the application of EK significantly (P<0.05) affected the distribution of sodium ions in both column lengths (Figures 4-5 and 4-6). In general, the sodium ions migrated towards the bottom electrode (i.e. cathode) with the bottom depth increasing by ~200 and ~400 mg L^{-1} Na after 168 h EK in the 30 cm and 50 cm columns, respectively (Figure 4-5). However, electrode separation distance in the different column lengths did affect the sodium distribution profile with EK application over time. For example, in the 30 cm column, the application of EK for periods < 48 h produced a reduction in sodium concentration at the bottom depth (Figure 4-5) but not in the 50 cm column (Figure 4-6). Similarly, there was generally a small increase in sodium concentration at intermediate depths during EK treatment in both columns. However, the 25 cm depth in the 50 cm column had a lower sodium concentration for all periods of EK application (Figure 4-6) which was not observed in the 30 cm column (Figure 4-5).

Figures 4-7 and 4-8 show the effect of sand column length and EK application time on chloride distribution within the sand columns. In general, chloride was found to migrate towards the upper electrode (i.e. anode) with increasing EK application period. For example, higher chloride concentrations were generally found at the 5 and 15 cm depths in both column lengths. Similarly, lower chloride concentrations were found near the bottom electrode (i.e. cathode) of these columns. However, differences were found due to electrode separation distance with a narrow transition zone (5 to 15 cm depth) between high and low chloride concentration observed in the 30 cm column (Figure 4-7) but a wider zone (15 to 35 cm depth) in the 50 cm columns (Figure 4-8). Hence, in the 50 cm columns, the middle depth (25 cm) had a chloride concentration that was similar to the initial level throughout the application of EK.

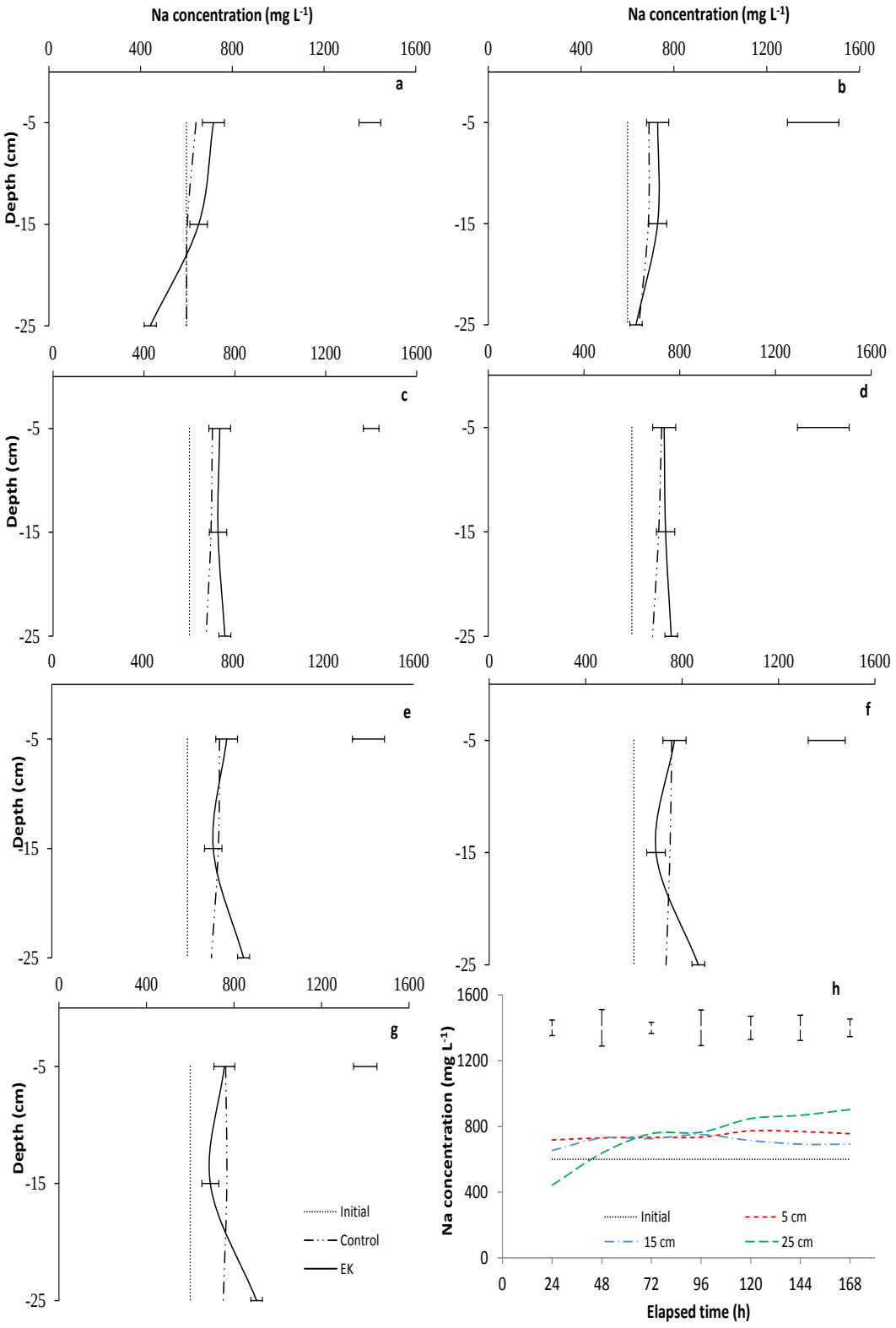

Figure 4-5: Solution sodium concentration [Na] in 30 cm columns where EK was applied at 0.01 A for (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h, (g) 168 h. Graph (h) shows the effect of EK application time. Horizontal and vertical bars show $LSD_{0.05}$.

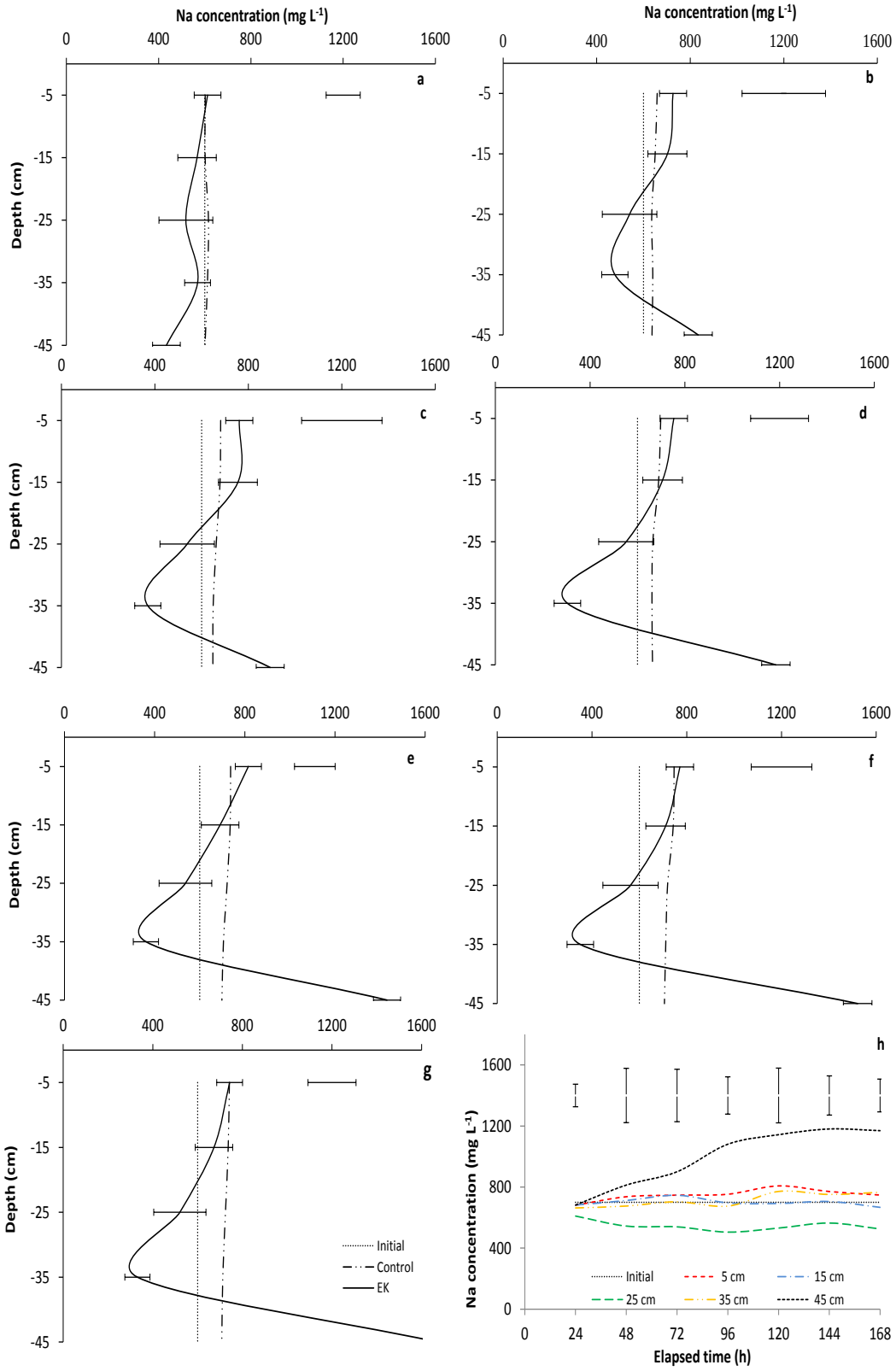

Figure 4-6: Solution sodium concentration [Na] in 50 cm columns where EK was applied at 0.01 A for (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h, (g) 168 h. Graph (h) shows the effect of EK application time. Horizontal and vertical bars show $LSD_{0.05}$.

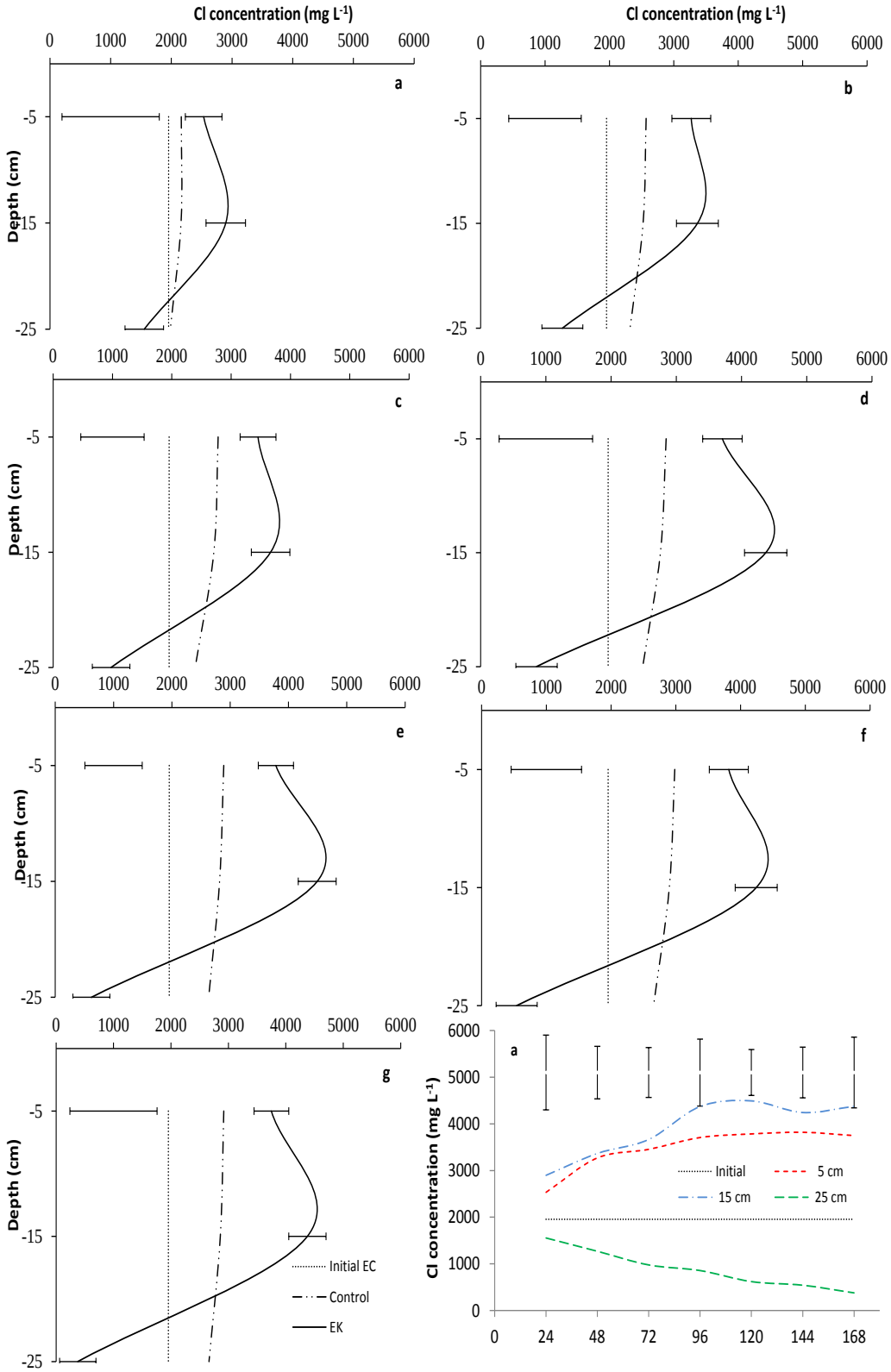

Figure 4-7: Solution chloride concentration [Cl] in 30 cm columns where EK was applied at 0.01 A for (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h, (g) 168 h. Graph (h) shows the effect of EK application time. Horizontal and vertical bars show $LSD_{0.05}$.

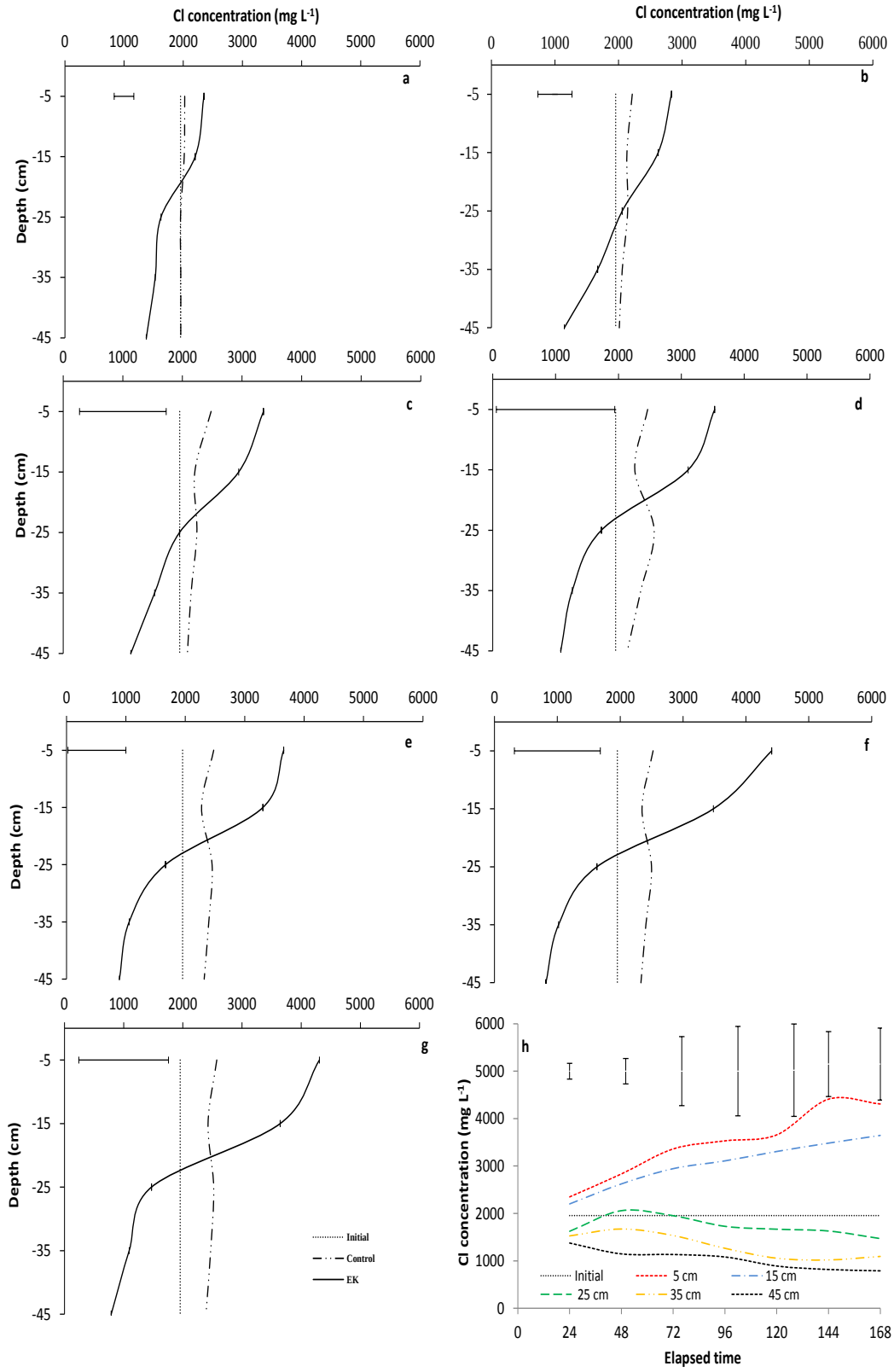

Figure 4-8: Solution chloride concentration [Cl] in 30 cm columns where EK was applied at 0.01 A for (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h, (g) 168 h. Graph (h) shows the effect of EK application time. Horizontal and vertical bars show $LSD_{0.05}$.

4.3.1.4 *Sand water content*

The initial and final gravimetric water content is shown in Figure 4-9. In general, the effect of gravitational drainage was significant in all columns with significantly lower moisture contents in the upper layers compared to the lower layers. There were only minor differences in water distribution due to the application of EK. In both column lengths, EK produced a non-significant decrease in water content in the upper layers (e.g. 5 and 15 cm depth in the 30 cm column, 10 and 20 cm depth in the 50 cm column) and a similar non-significant increase in water content at the slightly deeper layers (20 and 25 cm deep in the 30 cm column, 30 cm deep in the 50 cm column).

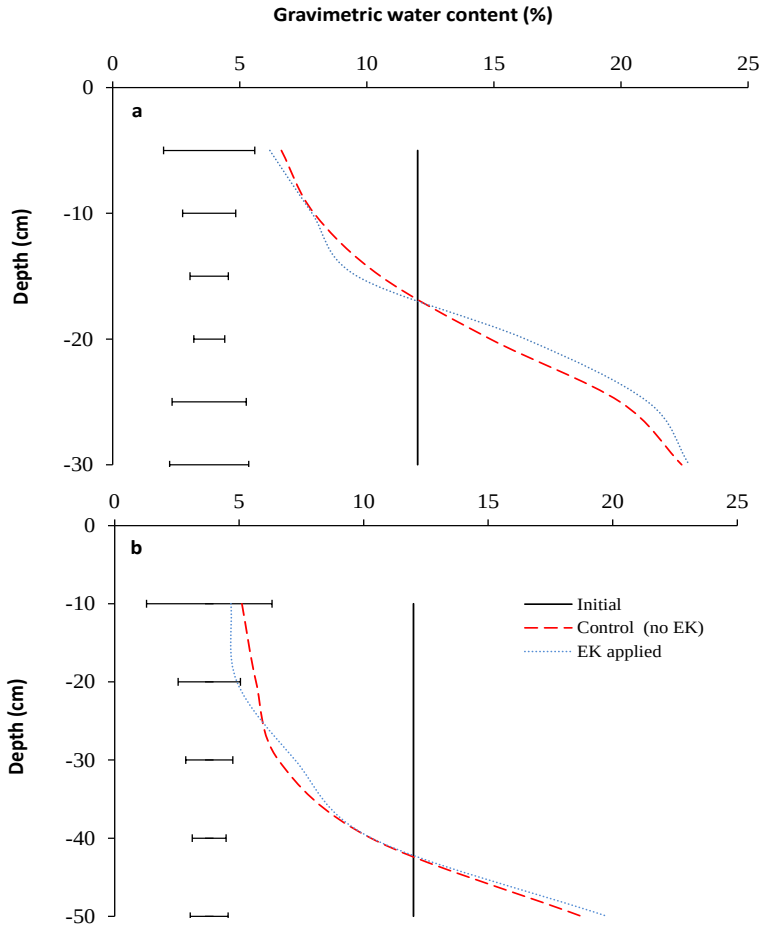

Figure 4-9: Effect of 0.01A EK application on gravimetric water content in (a) 30 cm and (b) 50 cm columns irrigated with saline-sodic water. Bars at the left of graph are LSD (α=0.05) for comparing water content between treatments.

4.3.2 Effect of current strength application rate

4.3.2.1 *Effect on solution electrical conductivity*

Increasing the rate of electrical current applied from 0.01A to 0.02A generally produced an increase in the rate and extent of salt movement due to EK within the sand column (Figure 4-10). However, significant (P<0.05) differences in electrical conductivity at specific depths were only observed after EK had been applied for at least 72 h. Slightly higher EC was observed near the anode (5 and 15 cm extraction depths) at periods up to 72 h and deeper (i.e. 25 cm) when 0.02A EK was applied for

>96 h. Similarly, 0.02A EK generally produced significantly lower EC in the bottom (45 cm) layer than the 0.01A EK treatment when applied for periods >72 h.

4.3.2.2 *Effect on pH*

Increasing the rate of EK application generally increased the rate at which the pH changed with the sand column (Figure 4-11). For example, the pH decreased to <3 near the anode (5 and 15 cm extraction depths) within 24 h of applying 0.02A but required >96 h of 0.01A EK to reach comparable levels. Significant differences in pH due to EK rate of application were only observed in the 5 and 15 cm depth at 24 h and the 25 cm depth at 48 h. While there was a general (but non-significant) trend for 0.02A EK to produce a slightly lower pH than 0.01A EK at depths ≤35 cm for all application periods. There were no significant pH differences observed in the bottom (45 cm) sand column layer due to the rate of EK applied.

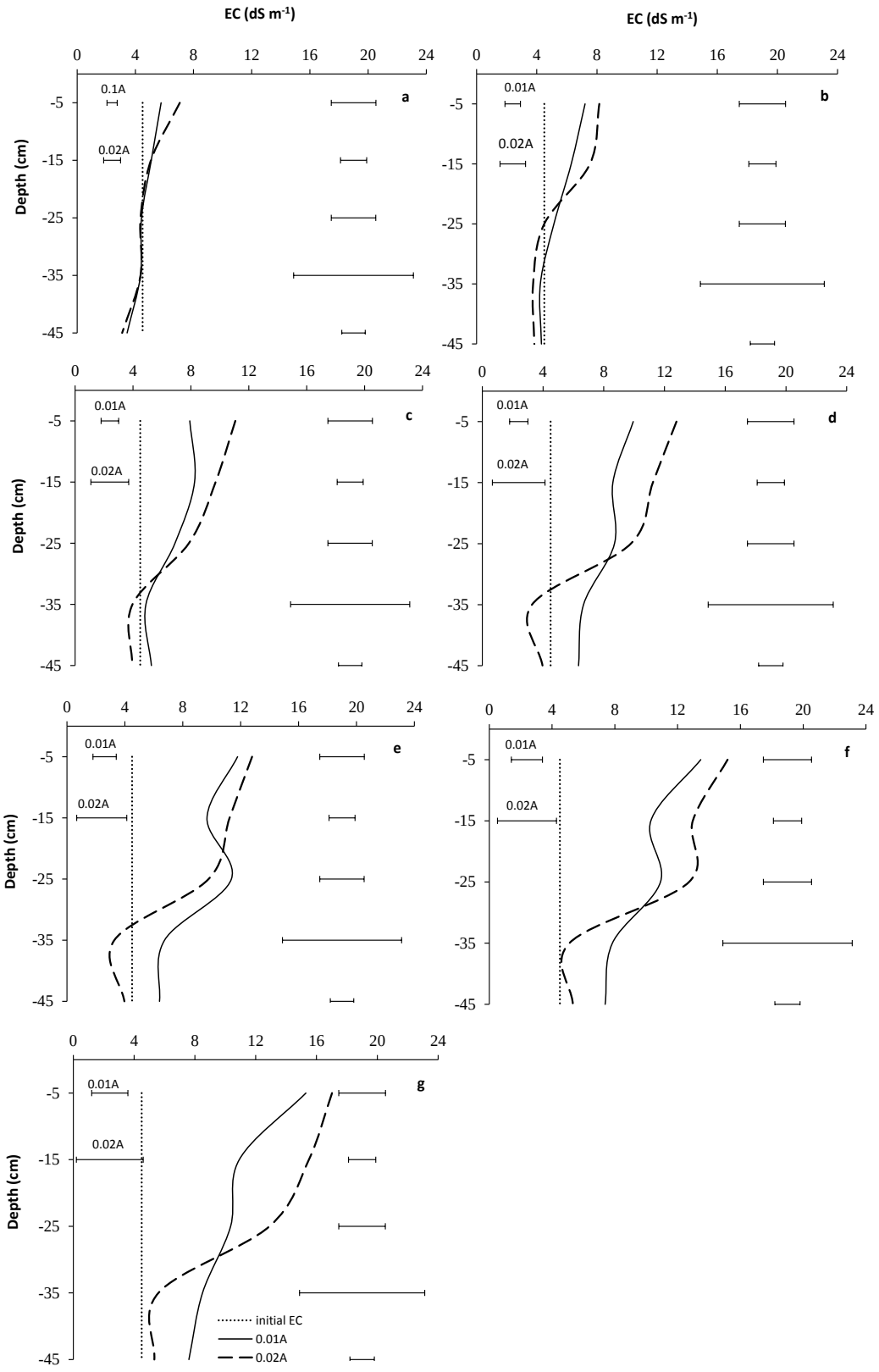

Figure 4-10: Solution electrical conductivity (EC) in 50 cm columns where EK applied at either 0.01A or 0.02 A for (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h, (g) 168 h. Bars at the right of graph are LSD (α=0.05) for comparing EC between treatments. Bars at the left of graph are LSD (α=0.05) for comparing within treatments.

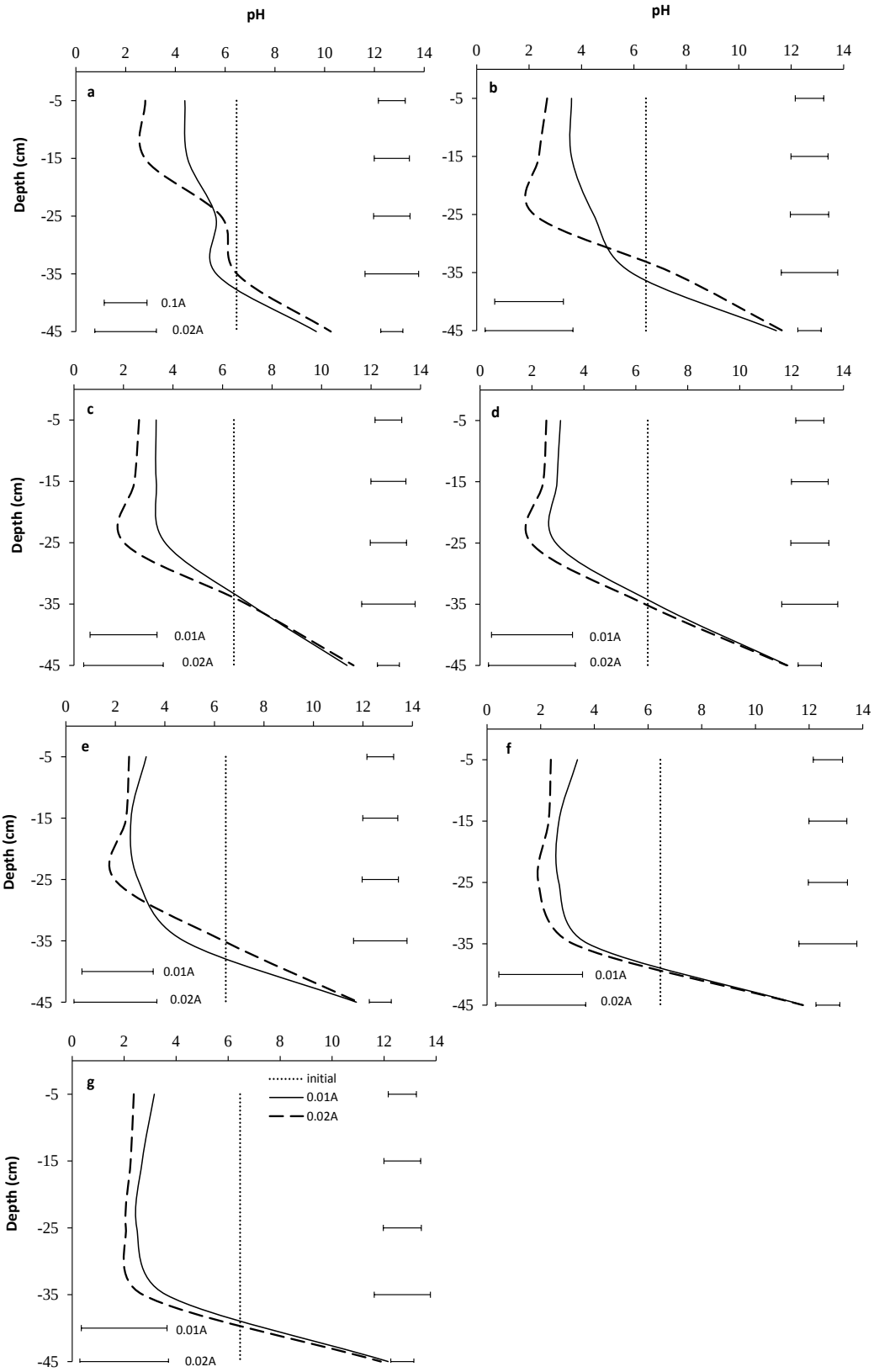

Figure 4-11: Solution pH in 50 cm columns where EK applied at either 0.01A or 0.02 A for (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h, (g) 168 h. Bars at the right of graph are LSD (α=0.05) for comparing pH between treatments. Bars at the left of graph are LSD (α=0.05) for comparing within treatments.

4.3.2.3 *Sodium and chloride concentration*

There were relatively small differences in the sodium distribution within the sand columns due to the effect of applying EK at either 0.01A or 0.02 A (Figure 4-12). In both treatments, increasing treatment time resulted in a significant ($P<0.05$) increase in the sodium concentration in the surface (5 and 15 cm) layers due to the application of saline-sodic irrigation water. Similarly, the application of EK resulted in the movement of sodium ions towards the cathode producing a small (non-significant) decrease in concentration in the middle depth of the column but a significant increase in the sodium concentration in the bottom (45 cm) column layer when EK had been applied for ≥48 h. The distance of sodium ion movement appeared to be influenced by the rate of EK application with the minimum sodium concentration observed at 25 cm depth in the 0.01A treatment but at 35 cm depth in the 0.02A treatment.

Figure 4-13 shows the effect of EK application rate on the distribution of chloride in the sand columns. In both treatments, the application of EK resulted in the movement of chloride ions from the bottom (35 and 45 cm) layers towards the surface (5 and 15 cm) soil layers. Hence, there was a significant increase in chloride concentration in the surface layers and a significant decrease in chloride concentration in the bottom layers. There was no significant difference in the distribution of chloride due to EK application rate at either short (<48 h) or long (>96 h) of application period. However, a significantly lower chloride concentration was observed at 35 cm depth in the 0.02 A (compared to 0.01A) after 72 and 96 h of application suggesting that the movement of the chloride ions towards the cathode occurred quicker when the higher rate of EK was applied.

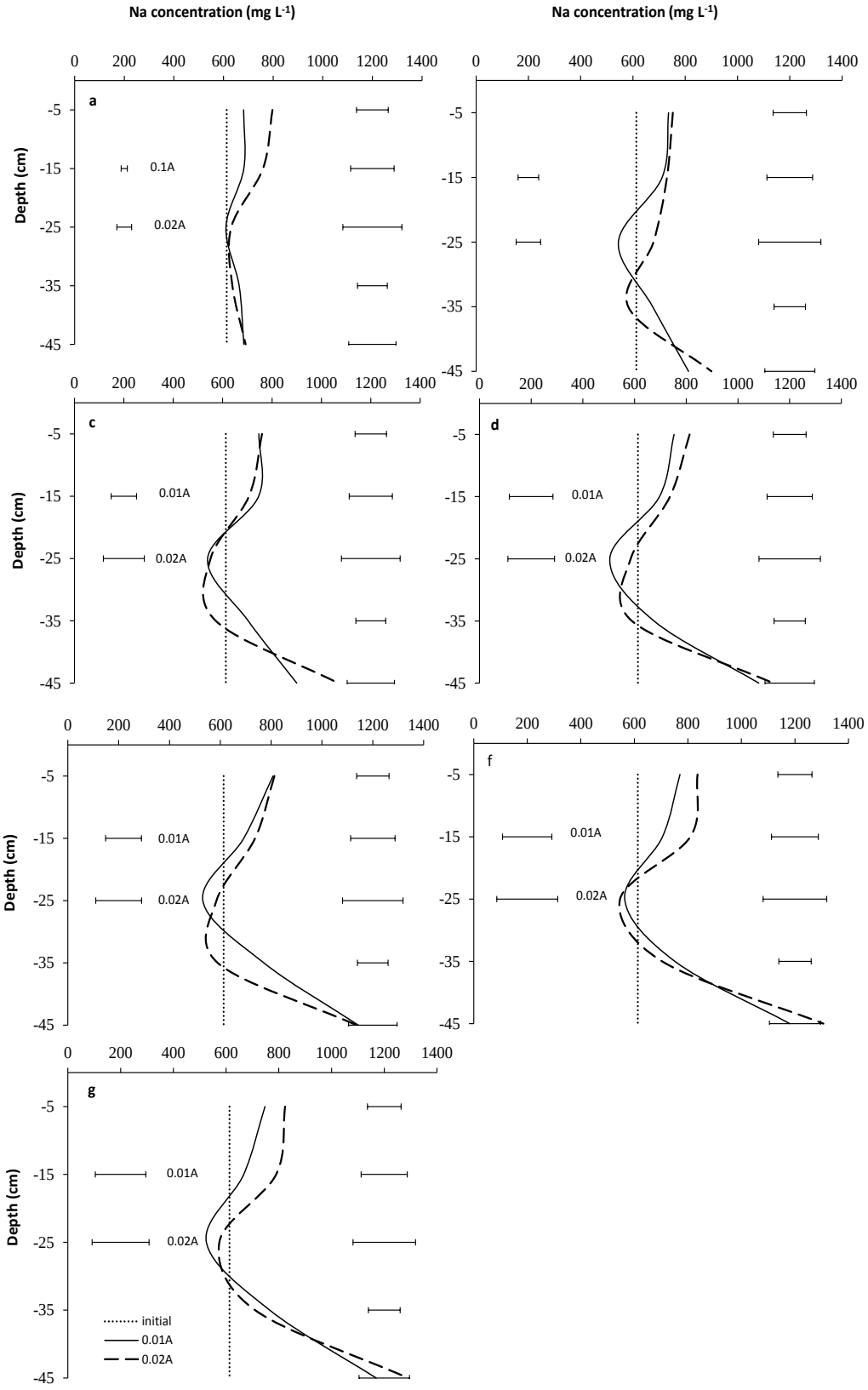

Figure 4-12: Solution sodium concentration in 50 cm columns with EK applied at 0.01A or 0.02 A for: (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h and (g) 168 h. Bars at the right of graph are LSD (α=0.05) for comparing [Na] between treatments. Bars at the left of graph are LSD (α=0.05) for comparing within treatments.

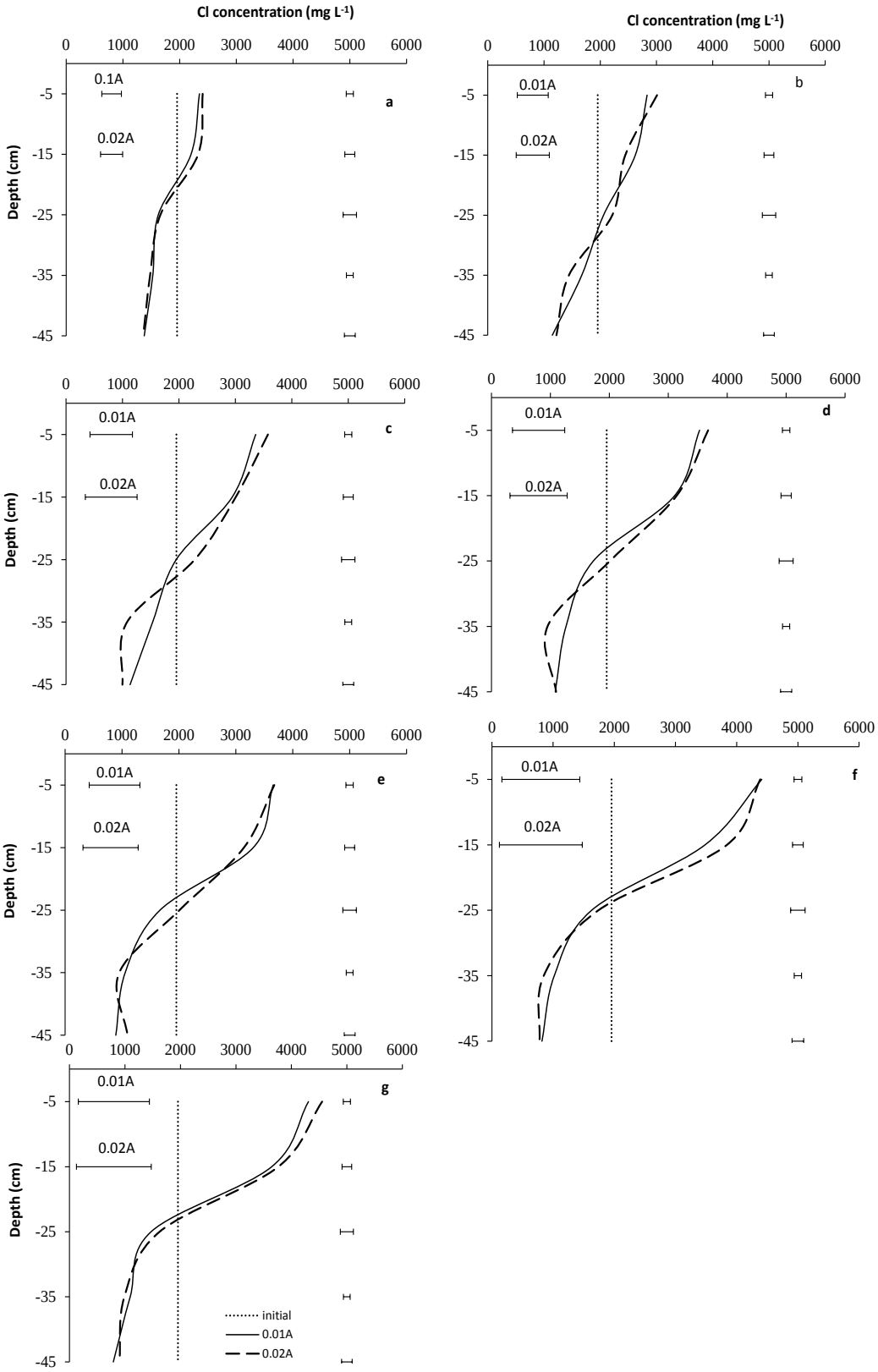

Figure 4-13: Solution chloride concentration in 50 cm columns with EK applied at 0.01A or 0.02 A for: (a) 24 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 120 h, (f) 144 h and (g) 168 h. Bars at the right of graph are LSD (α=0.05) for comparing between treatments. Bars at the left of graph are LSD (α=0.05) for comparing within treatments.

4.3.2.4 *Soil moisture content*

The effect of gravitational drainage was evident in both EK treatments with significantly lower final soil moisture contents in the upper column layers compared to the lower column soil layers (Figure 4-14). However, there was no significant (P<0.05) difference in the final soil moisture content within the sand columns at any depth due to the rate of EK application. A decreasing (non-significant) trend in moisture content was observed at 5 cm depth and non-significant increasing trend in soil moisture observed at deeper (25-35 cm) depth with increasing EK rate.

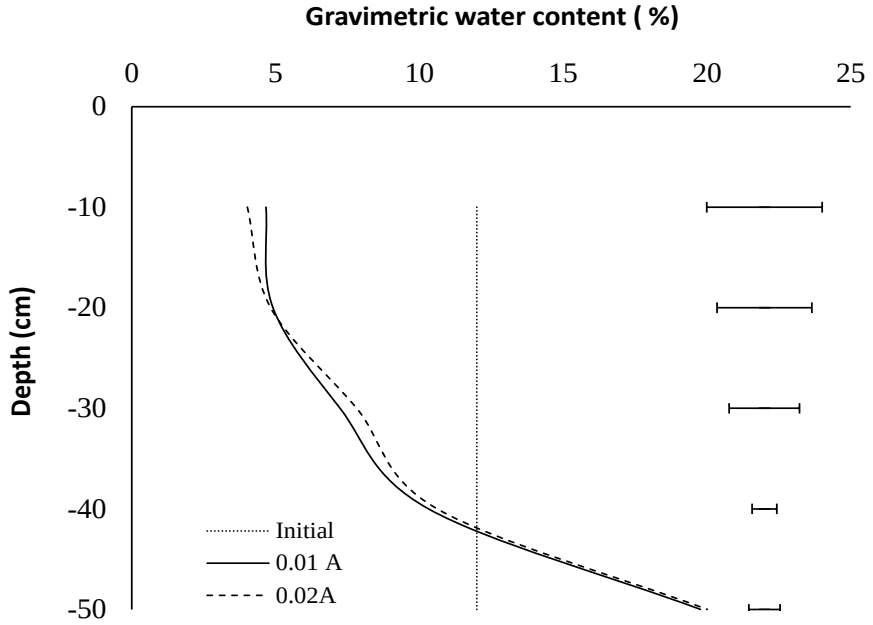

Figure 4-14: Effect of EK application rate on the gravimetric water content in a 50 cm column irrigated with saline-sodic water after EK applied for 168 h. Bars at the right of graph are LSD (α=0.05) for comparing the water content between treatments.

4.4 Discussion

The application of the combined EK and irrigation treatment generally resulted in a significant increase in the concentration of salt ions (as measured by EC) at the surface (anode) electrode and a comparatively smaller increase at the bottom of the column where the cathode was located (e.g. Figure 4-1, 4-2 & 4-10). However, this is not consistent with the results observed by Huweg (2013) who reported that the application of EK (5 mA for ≥45 h) on a horizontal sandy soil column produced a significant increase in EC adjacent to both the cathode and anode while it reduced EC in the middle of the soil column.

By applying an electric potential to a soil-water system, ions (solutes) move towards the opposite charged electrode due to electro-migration transport processes (Section 2.6.3). The positively-charged ions (cations) move towards the cathode (negatively-charged) while the negatively charged ions (anions) move towards the anode (positively-charged). This movement should result in a decrease in salt levels in the middle of the column and the accumulation of salts near both electrodes (Mattson et al. 2002; Reddy & Cameselle 2009). However, the expected accumulation of salts

near the cathode (bottom of the column) was not observed in the current experiment (Figures 4-1, 4-2 & 4-10). This is most likely because the column was mounted vertically, irrigated during the EK treatment and allowed to free-drain from the base of the column. In this case, any salts that were attracted towards the cathode and would have accumulated adjacent to the cathode due to the EK were leached from the column. Similarly, the EC in the middle of the column was not smaller than the EC measured at the bottom of the column because the downward movement of the applied irrigation water moved salts from the surface layer into this zone in the middle of the column.

The change in EC near the electrodes occurred faster when the amount of electricity applied (current and duration) was increased (e.g. Figures 4-1, 4-2 & 4-10). The rate of salt accumulation at the anode increased from the initial value (4.5 dS m^{-1}) to reach 6 and 8 dS m^{-1}after 72 and 24 hours applying 0.01A and 0.02A, respectively. However, in depths 35 and 45 cm, the EC was less than initial value when 0.01A and 0.02A were applied over 48 and 120 hours, respectively. This is consistent with Cho (2009) who found that increasing the current density increased the rate of salt removal.

The effect of EK on the movement of specific ions was consistent with electro-migration theory (Section 2.6.3). Chloride (an anion) was attracted towards the anode (surface) and sodium (a cation) was attracted towards the cathode (bottom). In both cases, the concentration profiles suggested that the EK not only moved the ions but held them adjacent to the electrode even with the downward movement of the irrigation water. For example, the sodium concentration was higher adjacent to the cathode (Figure 4-12) even though the EC of the bottom column layer was lower due to salt leaching and drainage (Figure 4-10). Similarly, the chloride concentration was higher adjacent to the anode (surface) than at any other location in the column (Figure 4-13) even though the applied irrigation water leached other salts downward.

The soil pH adjacent to the electrodes was rapidly and significantly altered by EK application (Figures 4-3, 4-4 & 4-11). The effect was consistent with the expected oxidation and reduction (electrolysis) processes occurring at the electrodes (Section 2.6.1) with pH decreased near the anode (surface) due to the generation of H^+ ions and increased near the cathode (bottom) due to generation of OH^- ions. The pH at the anode was generally highly acidic (<4) while the area adjacent to the cathode was highly basic (~12). In both cases, these extreme pH values could be expected to have an impact on the availability (and solubility) of other ions in the solution and adversely affect plant root growth. The acidic region generated near the anode (surface) was observed (e.g. Figure 4-11) to migrate downwards in the column (presumably due to electro-osmosis, electro-migration, diffusion and/or gravitational drainage). The highly acidic pH extended throughout the sand column (except for within 10 cm of the cathode) after only 48 h of EK in the short (30 cm columns) but required longer (e.g. >96 h) EK in the longer (50 cm columns). In contrast, the region of basic pH generated adjacent to the cathode did not advance far (<10 cm) from the cathode in either column length possibly because of the downward movement of the irrigation water restricting the migration of OH^- ions upward from the cathode.

The main effect of increasing the distance between the electrodes was to increase the EK application period required to reach an equilibrium salt or pH profile within the column. Hence, at shorter (<48 h) periods of EK application in the longer (50 cm) column there was a generally a middle zone of the column which was not affected by significant changes in EC or pH. Hence, the length of the sand column and period

over which EK is applied could be expected to be a major determinant of the effectiveness of the EK in moving salts out of the profile and the relative proportion of the sand column which may be adversely affected by extreme pH values. Increasing the rate of EK generally resulted in the equilibrium salt and pH profile being reached quicker but with only relatively minor differences in the longer term EC or pH profile within the column.

4.5 Conclusion

This preliminary experiment has shown that the application of an electrical field to an irrigated sand column can significantly affect both soil solution ion movement within the column and the soil pH near the electrodes (due to electro-chemical reactions at the electrodes). Similarly, specific ion movement due to EK was also found to vary, possibly due to differences in ion mobility. However, the magnitude of the effect on both the distribution of the salts and soil pH within the sand column was found to vary as a function of the period of EK application, rate of EK application and the distance between the electrodes. The application of irrigation water during the EK treatments also affected the ion movement within the columns.

A key design and management objective for an irrigated root zone involving the application of EK is that the soil solution should be maintained within a range of EC, soil pH and individual specific ion concentration values which are non-toxic to plant roots. This research has shown that the application of EK at higher rates, longer periods, or in short columns is more likely to create adverse soil solution conditions. Hence, in this research, the most favourable root zone conditions were generally observed when 0.01A was applied for periods < 48 h on the longer (50 cm) columns.

While the effects of EK application have been demonstrated in this study, further research is required to better understand the quantitative relationships between the irrigation soil-water movement dynamics and the ability to design and manage an EK system to provide practical benefits. One clear practical benefit would be the ability to use EK to retain important soil nutrients within the root zone while increasing the efficiency of salt leaching from the bottom of the profile.

This work has shown that anions (i.e. chloride in this work) can be moved upwards in a sand column and held in the upper soil layers against the downward flow of applied irrigation water. However, there is a need to evaluate the potential to control the movement of anionic macro-nutrients (e.g. nitrate) within the root zone. This topic is explored further in chapter 5.

Chapter 5: An evaluation of the potential to use electro-kinesis for controlling nitrate movement in an irrigated sand column

5.1 Introduction

Nitrogen is an essential plant nutrient and a major determinant of economic crop yields. Hence, efficient nitrogen management will be important to meet the increasing global demand for food and ensure food security. However, nitrate-nitrogen (the main for in which plants absorb N) is highly soluble and moves readily with soil-water, potentially leading to the loss of N from the root zone. N losses may be exacerbated by excessive water application (through irrigation or precipitation) and the application of fertiliser rates greater than the nutrient requirement of the crop. The timing of nutrient application during the season relative to plant needs and water application is also important. In high rainfall areas or under irrigated conditions, particularly on sandy soils, there is often subsoil drainage of water through the soil and consequent leaching of nitrate from the root zone leading to economic and environmental impacts (Mitsch & Day Jr 2006). In these cases, there are often difficulties maintaining nitrogen in the root zone (Nielsen et al. 1982) and improved methods to manage and retain nitrogen within the root zone are required.

Electro-kinesis (EK) has been shown to influence the movement of ions in solutions and within porous media (Budhu et al. 1997; Cairo et al. 1996; Chen et al. 1999; Jia et al. 2005). This was supported by the preliminary evaluation of EK (Chapter 4) which demonstrated that it was possible to control both cation and anion movement in an irrigated sand column. In this work, the anode was located near the surface of an irrigated sand column and chloride (an anion) was found to migrate towards the anode (Section 4.3.1.3). Hence, a relatively high concentration of chloride was maintained in the upper sand column when EK was applied even though the application of irrigation water and movement of the soil-water due to gravitational forces would normally have redistributed these ions to lower sand column layers and/or leached the chloride from the profile. As nitrate is also an anion, these findings suggest that it may be possible to use EK to reduce nitrate leaching from an irrigated soil.

Several studies (e.g. Cairo et al. 1996; Jia et al. 2005) have found that applying an electrical field to a soil under field conditions significantly increased nitrate concentration near the anode. Eid et al. (2000) found a similar result under laboratory conditions. However, while these studies confirm that nitrate retention in root zones using EK is possible, there is little information on the effect of EK application rate on nitrate retention and in particular, the effect of EK on N retention when irrigation water is applied under different conditions. This information is required to develop guidelines for the effective use of EK to control N losses from irrigated soils. Hence, the work reported in this chapter investigates the effect of EK application rate on nitrate retention in an irrigated sand column as well as the interaction between N movement and the rate of irrigation water application when EK is applied.

5.2 Material and methods

Two separate experiments were conducted in this trial. The first experiment investigated the effect of different EK application rates on nitrate movement within sand columns. No irrigation water was applied to the sand columns during the first experiment. The second experiment investigated the effect of different irrigation water

application rates on nitrate retention when a fixed rate of EK was applied to the columns.

For both experiments, 50 cm long columns fitted with carbon fibre electrodes were prepared and filled with sand using the method described in Section 3.2. Prior to packing, the sand was wetted to 12 % gravimetric moisture content using a 1600 mg L^{-1} nitrate (NO_3^-) solution prepared using distilled water and calcium nitrate tetra hydrate ($Ca(NO_3^-)_2.4H_2O$). The columns were packed to a bulk density (ρ_b) of 1.5 g cm^{-3} and soil solution extraction tubes were installed (Section 3.2) in the middle of the sand columns at 5, 15, 25, 35 and 45 cm depth.

For the second experiment, a plastic container was filled with rain water (EC = 0.016 ± 0.02 dS m^{-1}, pH = 7 ± 0.04) and placed above the vertical sand columns to provide water for drip irrigation using the method described in section 3.3. Water was applied to the sand columns at a rate of 10, 20 and 30 mL h^{-1} for 9 h (Equivalent of 12, 23 and 35 mm of rainfall, respectively) from the initiation of the treatment.

Four strengths of electric current (0, 0.005A, 0.01A and 0.02A) were evaluated in each experiment with the electrical field generated using the apparatus and setup described in section 3.4. The EK was applied continuously for a total of 24 h in both experiments and two replications of each EK treatment were conducted.

Soil solution samples (section 3.3) were extracted after 3, 9 and 24 h of EK application in first experiment and after 3, 9, 12 and 24 h of EK application in the second experiment. The electrical conductivity, pH and nitrate concentration were measured using the methods reported in section 3.5.

Data are expressed as the mean of two replicate values for each measured parameter. Statistical analyses were undertaken using Statistical Package for the Social Sciences (SPSS) v19 for Windows 7 (Cramer 2004). Analyses involved univariate ANOVA. Two-Way ANOVA was used to study the effect of current and duration of application on solute movement and to study the interaction between electro-kinesis solute dynamics and irrigation at 3 and 9h. One-Way ANOVA was used to compare the effect of EK application for the 24 h period (between the 9 and 24 h measurements there was no additional water applied but EK was applied). Least significant difference (LSD) was used to compare the means at a probability level of 5 %.

5.3 Results

5.3.1 Solute dynamics due to the rate and duration of EK application

The application of EK was found to move nitrate from deeper layers (35-45 cm) to the 15-35 cm layer in the sand column (Figure 5-1). Increasing the rate of EK application resulted in a small but significant increase in the amount of nitrate that was moved. The control (no-EK) treatment demonstrated that nitrate migrated from the surface to deeper column layers over time (Figure 5-1). This produced a significantly lower nitrate concentration (~1200 mg L^{-1}) at the surface (5 cm) compared to the concentration (~1700 mg L^{-1}) at the bottom (45 cm) of the column after 24 hours of drainage.

Significant differences in the nitrate concentration profiles between the control and EK treatments only became apparent after 9 hours of EK application (Figure 5-1b). This difference was most marked at the 45 cm depth where nitrate concentration in the

control treatment had increased from the initial condition but had decreased under the application of EK. After 24 hours of EK application, the nitrate concentration in the 5-25 cm depths were generally 150-300 mg L^{-1} higher than the control treatment while the concentrations at 45 cm in the EK treatment columns was approximately 500-600 mg L^{-1} lower than the concentration observed in the control columns (Figure 5-1c).

The distribution of the salt within the sand columns was affected by EK application (Figure 5-2). It is clear that increasing the EK power applied leads to greater salt movement toward the surface (anode) resulting in an increased electrical conductivity (EC) throughout the sand column, except for the 45 cm depth near the cathode (this is the washed electrode). Small but significant differences in EC were observed at some depths within 3 h of applying EK (Figure 5-2b), but larger significant differences were apparent at all depths after 9 h (Figure 5-2b). For example, the EC at 15 cm after 9 h EK was 2.8, 3.1 and 3.6 dS m^{-1} (Figure 5-2b) while at 45 cm depth it was 2.3, 2.0 and 1.6 dS m^{-1} for the 0.005A, 0.01A and 0.02A treatments, respectively. The differences in the EC profiles were greater after 24 h of EK application (Figure 5-2c).

Solution pH was highly sensitive to increases in the rate of EK applied to the columns (Figure 5-3). In general, the solution pH became more acidic near the anode and more alkaline near the cathode, with the effect increasing with rate and duration of EK application. There was no significant difference in pH after 3 h of EK (Figure 5-3a). However, the 5-15 cm depth in the 0.02A EK treatment approached a pH of 4 after 9 h of EK application while a pH of 5-6 was observed in the other EK treatments (Figure 5-3b). This trend continued with increasing duration of EK and a pH of 3-4 was observed for the 5-25 cm depth in the 0.02A treatment after 24 hours (Figure 5-3c). Only a small increase in pH (7-7.5) at the 45 cm depth was observed after 9 hours of EK but the pH was ~10 in all EK treatments after 24 hours of EK application (Figure 5-3c).

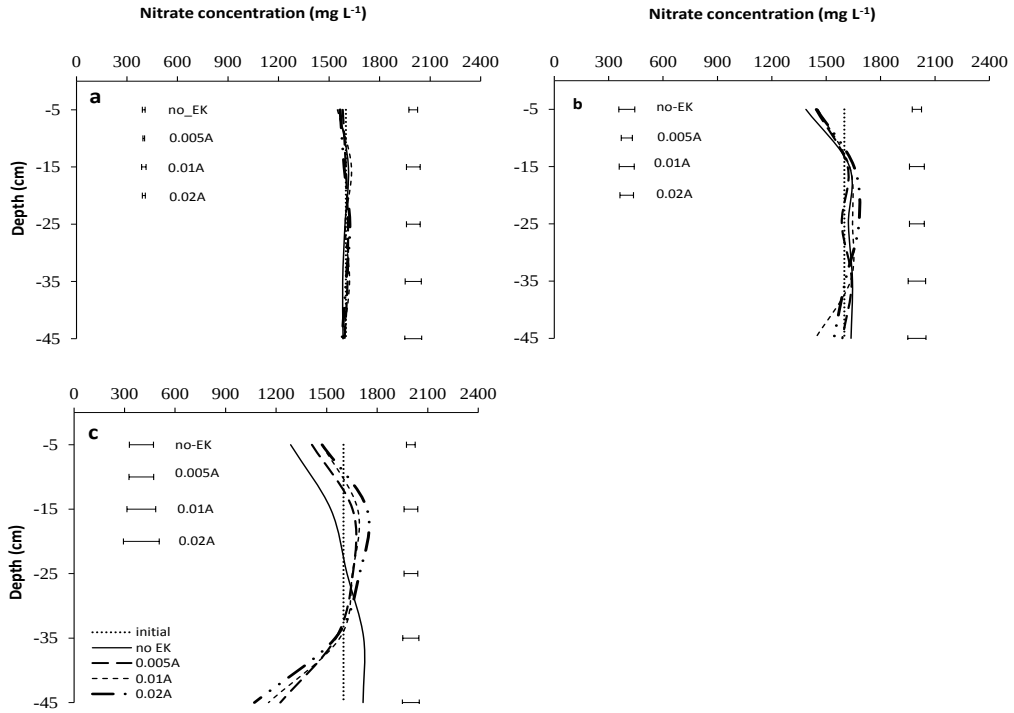

Figure 5-1: Nitrate concentration with depth after application of EK treatments and a non-EK (control) treatment for: (a) 3 h, (b) 9 h, and (c) 24 h. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments.

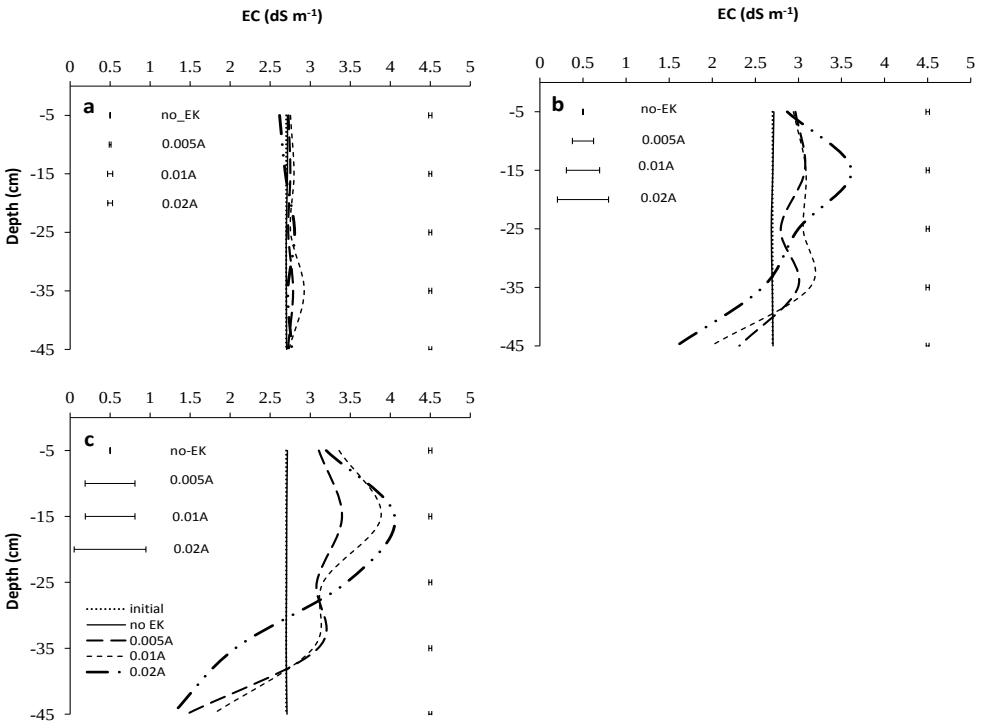

Figure 5-2: Electric conductivity (EC) with depth after application of EK treatments and a non-EK (control) treatment for: (a) 3 h, (b) 9 h, and (c) 24 h. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments.

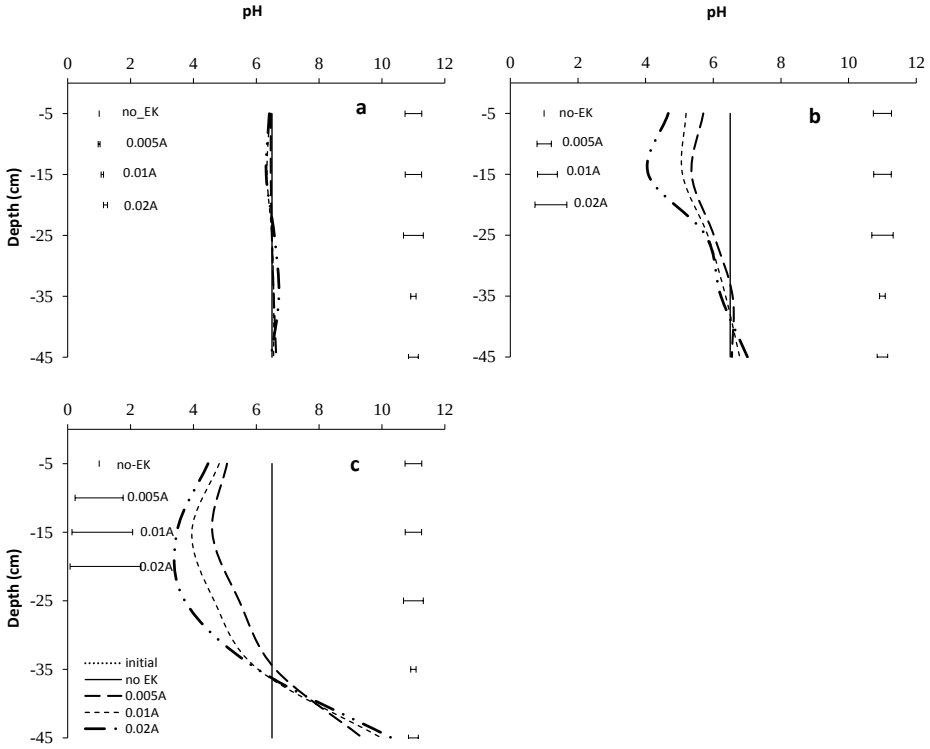

Figure 5-3: pH with depth after application of EK treatments and a non-EK (control) treatment for: (a) 3 h, (b) 9 h, and (c) 24 h. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments.

5.3.2 Effect of electro-kinesis and irrigation interactions on solute dynamics

Both the EK and drip irrigation applications were found to affect the movement of nitrate within the sand columns (Figures 5-4 to 5-6). Where there was no EK or

irrigation applied (Figures 5-4a to 5-6a) the nitrate concentration decreased from 1600 to ~1200 mg L^{-1} at 5 cm depth and increased from 1600 to ~1750 mg L^{-1} at 45 cm depth over the 24 hour treatment period. Application of irrigation (which only occurred for the first 9 hours of treatment) resulted in an increase in nitrate migration down the columns (Figures 5-4 to 5-6) and an increase in drainage from the columns (Table 5-1). Increases in irrigation application rate and duration both increased the depth of nitrate migration (via convective flow). For example, applying irrigation (all rates) without EK produced a nitrate concentration of <100 mg L^{-1} at 5 cm depth after 9 hours (Figure 5-5b-d). However, at 15 cm there was a significant difference in nitrate concentrations with ~1200, 600 and 240 mg L^{-1} observed for the 10, 20 and 30 mL irrigation applications after 9 hours (Figure 5-5b-d).

Table 5-1: The cumulative volume of leachate and concentration of nitrate over the 24 treatment period

	No flux		10 mL h^{-1}		20mL h^{-1}		30mL h^{-1}	
	Exit water (mL)	NO_3 (mg L^{-1})	Exit water (mL)	NO_3 (mg L^{-1})	Exit water (mL)	NO_3 (mg L^{-1})	Exit water (mL)	NO_3 (mg L^{-1})
Control (no EK)	79±9	1654±38	143±9	1646±39	169±12	1657±28	219±11	1540±41
0.005A	82±11	1596±26	163±14	1623±27	176±19	1636±24	244±14	1542±44
0.01A	80±7	1589±36	171±19	1626±31	187±14	1673±19	247±18	1534±58
0.02A	79±9	1592±48	165±13	1611±18	184±11	1686±29	251±17	1588±27

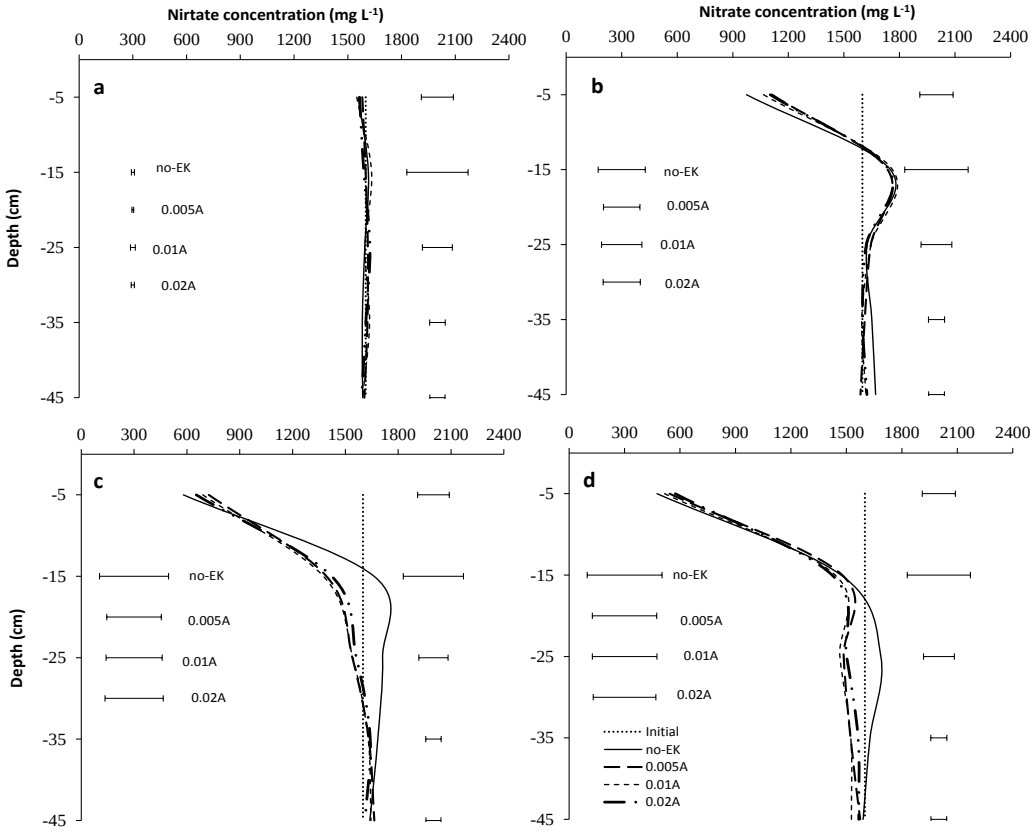

Figure 5-4: Nitrate concentration with depth after application of EK for 3 h on columns irrigated at either: a) 0, b) 10, c) 20 and d) 30 mL h^{-1}. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments.

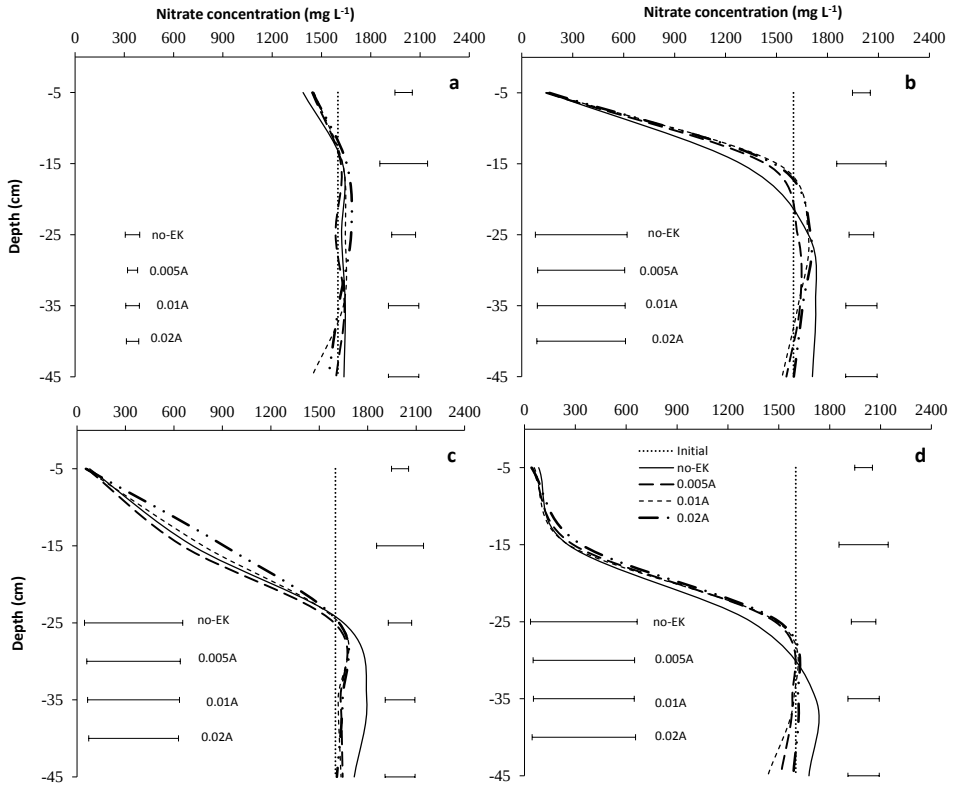

Figure 5-5: Nitrate concentration with depth after application of EK for 9 h on columns irrigated at either: a) 0, b) 10, c) 20 and d) 30 mL h^{-1}. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments

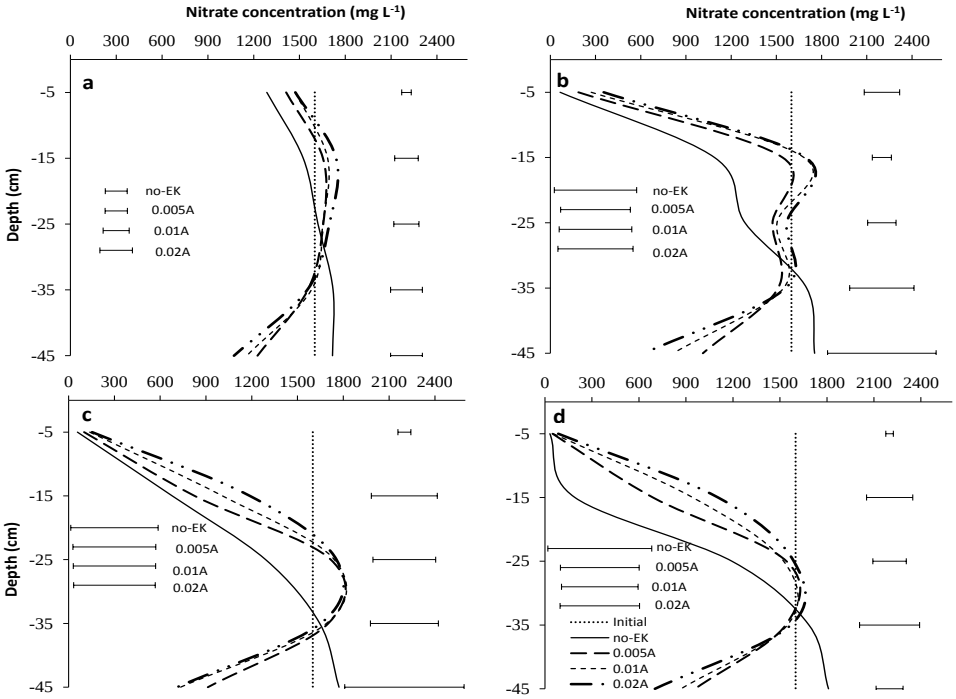

Figure 5-6: Nitrate concentration with depth after application of EK for 24 hours on columns irrigated for 9 h at either: a) 0, b) 10, c) 20 and d) 30 mL h^{-1}. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments

The application of EK generally resulted in the movement of nitrate towards the surface with the effect most noticeable either when irrigation was not applied (Figures 5-4a to 5-6a) or after the irrigation had been stopped (i.e. compare Figure 5-5 and 5-6). For example, after 24 hours of EK application where irrigation was not applied (Figure 5-6a) there was a significantly higher nitrate concentration at 5 and 15 cm (compared to the no-EK treatment) and a significantly lower concentration at 45 cm.

The movement of nitrate downwards in the sand columns while irrigation was occurring tended to overshadow the ability of the EK application to retain or move nitrate upwards in the columns. Hence, during the first 9 hours in which irrigation was applied (Figures 5-4 and Figures 5-5) there was generally no significant difference in nitrate concentration at any depth in the column due to EK. Similarly, there was generally no significant difference in either the volume or nitrate concentration of the drainage water from the columns (Table 5-1). However, after the irrigation application had been stopped, the continued application of EK resulted in significantly higher nitrate concentrations in the 15 to 35 cm depths and a significantly lower concentration at 45 cm (Figure 5-6).

The 0.02A EK treatment produced a small but generally non-significant increase in nitrate concentration compared to the 0.005A EK treatment at 5 and 15 cm depth for the 20 and 30 mL irrigation treatments (Figure 5-6c&d). However, the application of EK and increasing EK rate produced a significant increase in the total amount of nitrate found in solution extracted from the 0-25 cm depth when irrigation was applied (Figure 5-7). For example, 162 mg of nitrate was measured in the 0-25 cm depth of the no-EK treatment when 30 mL h^{-1} irrigation was applied but 310 mg of nitrate was measured when 0.02A EK had been applied (Figure 5-7).

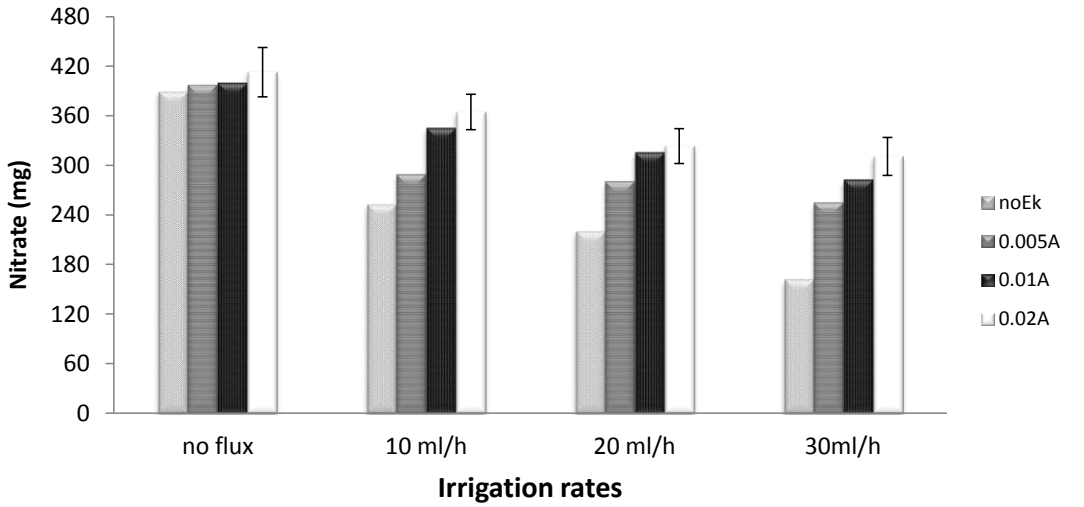

Figure 5-7: Total amount of nitrate in solution extracted from the 0-25 cm depth of the sand columns after application of the irrigation and EK treatments.

The EK and irrigation applications both significantly affected the salt distribution within the sand columns (Figures 5-8 to 5-10). The application of the irrigation during the first 9 hours (Figure 5-9) produced a decrease in EC in the surface layers (5 to 15 cm) and an increase in EC at 25 to 45 cm depth. It is clear that salts moved from the surface to the subsurface with water movement and the movement increased with both irrigation rate and duration. The application of EK generally tended to hold or move salts upwards in the sand column. For example, a significantly higher EC was observed at the 25 to 45 cm depth for the 0.02A EK treatment compared to the no EK treatment for the 20 and 30 mL h^{-1} irrigation treatments after 9 hours (Figure 5-9c&d). Similarly, applying EK after the irrigation was ceased (Figure 5-10) generally produced a decrease in EC at 45 cm depth and an increase in EC at 5 and 15 cm depth, with the effect greater with increasing rate of EK.

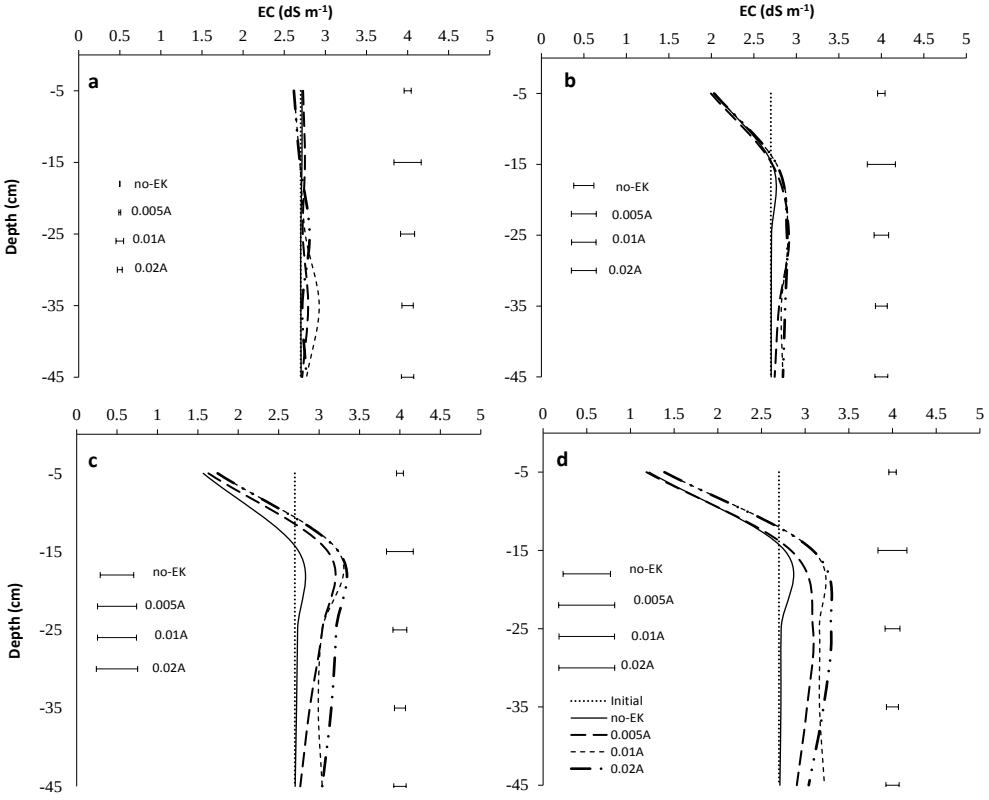

Figure 5-8: EC after application of EK for 3 h on columns irrigated with: (a) 0, (b) 10, c) 20 and (d) 30 mL h^{-1}. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments.

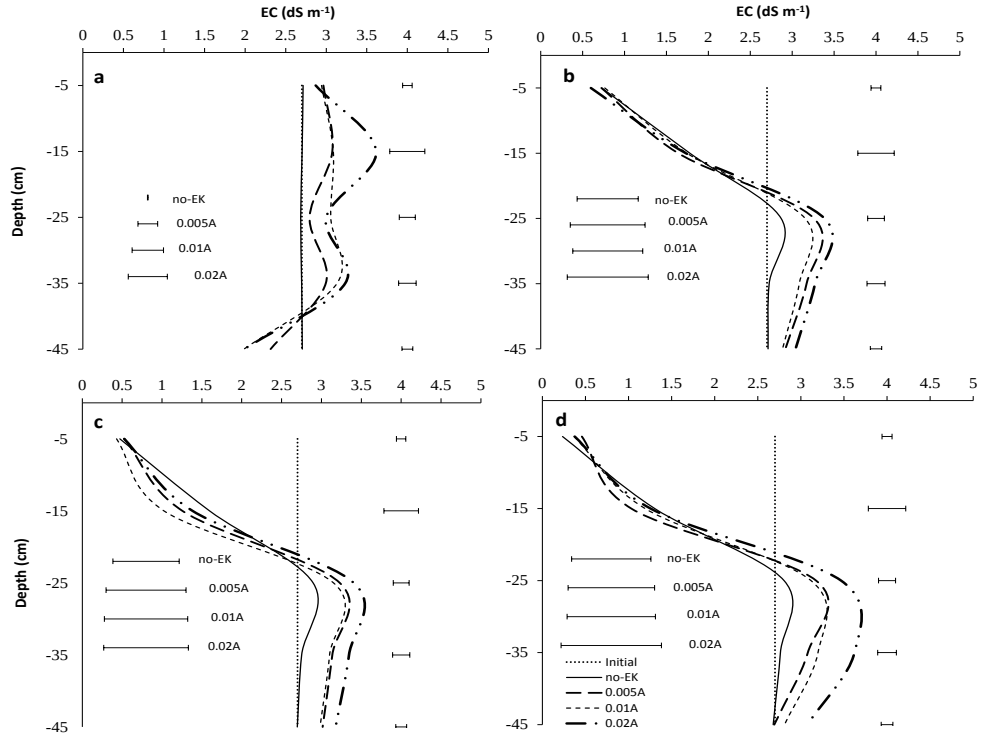

Figure 5-9: EC after application of EK for 9 h on columns irrigated with: (a) 0, (b) 10, (c) 20 and (d) 30 mL h^{-1}. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments.

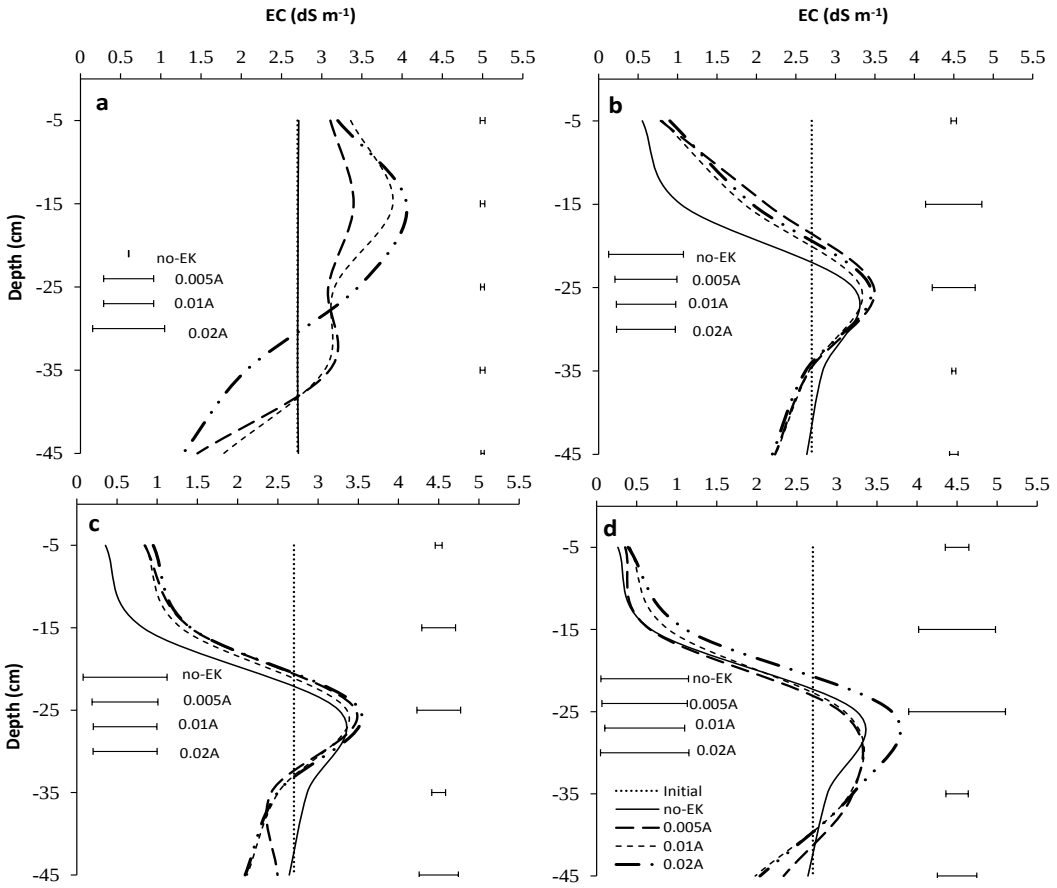

Figure 5-10: EC after application of EK for 24 h on columns irrigated for 9 h with: (a) 0, (b) 10, (c) 20 and (d) 30 mL h^{-1}. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments.

The application of EK significantly affected the pH observed within the sand column (Figure 5-13). However, pH changes were heavily buffered during the period of irrigation (Figures 5-11 and 5-12). Significant, but relatively small, decreases in pH were only observed at 25 to 45 cm for the 20 and 30 mL h^{-1} treatments during irrigation (Figure 5-11c&d, 5-12c&d). However, after irrigation had ceased (Figure 5-13), the application of EK increased the pH at the bottom of the column (45 cm) to greater than 9 but in the surface decreased only to between pH 5 and 6. At 25 cm depth, the pH ranged from ~5 in the 10 mL h^{-1} treatment to <3 in the 30 mL h^{-1} treatment (Figure 5-13).

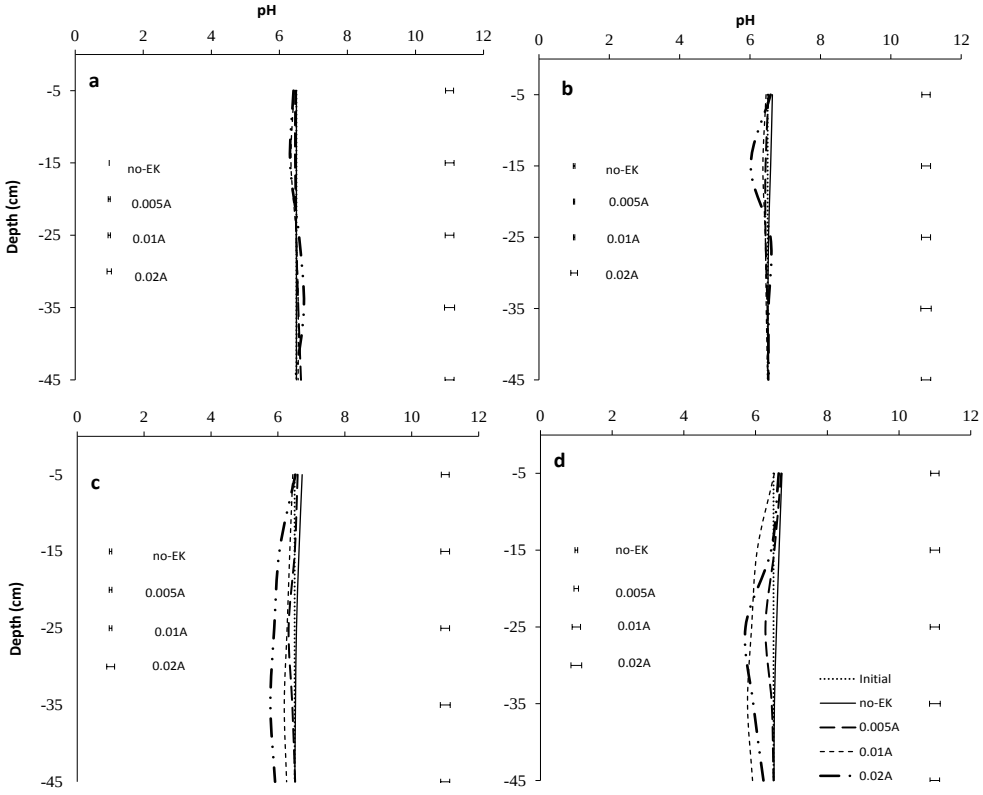

Figure 5-11: pH after application of EK for 3 h on columns irrigated with: (a) 0, (b) 10, (c) 20 and (d) 30 mL h^{-1}. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments

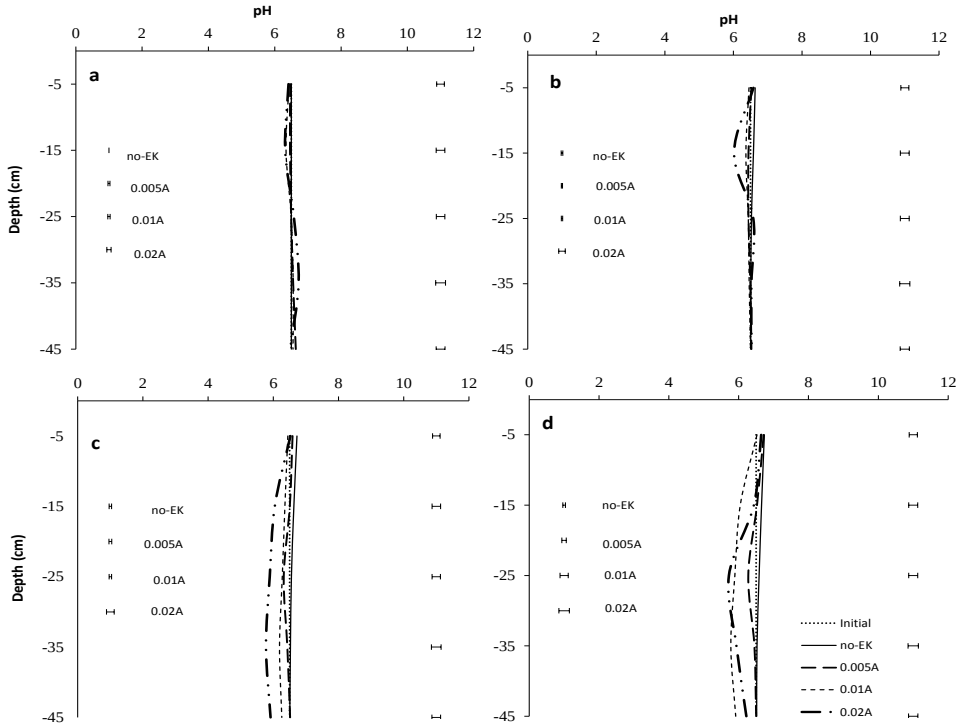

Figure 5-12: pH after application of EK for 9 h on columns irrigated with: (a) 0, (b) 10, (c) 20 and (d) 30 mL h^{-1}. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments.

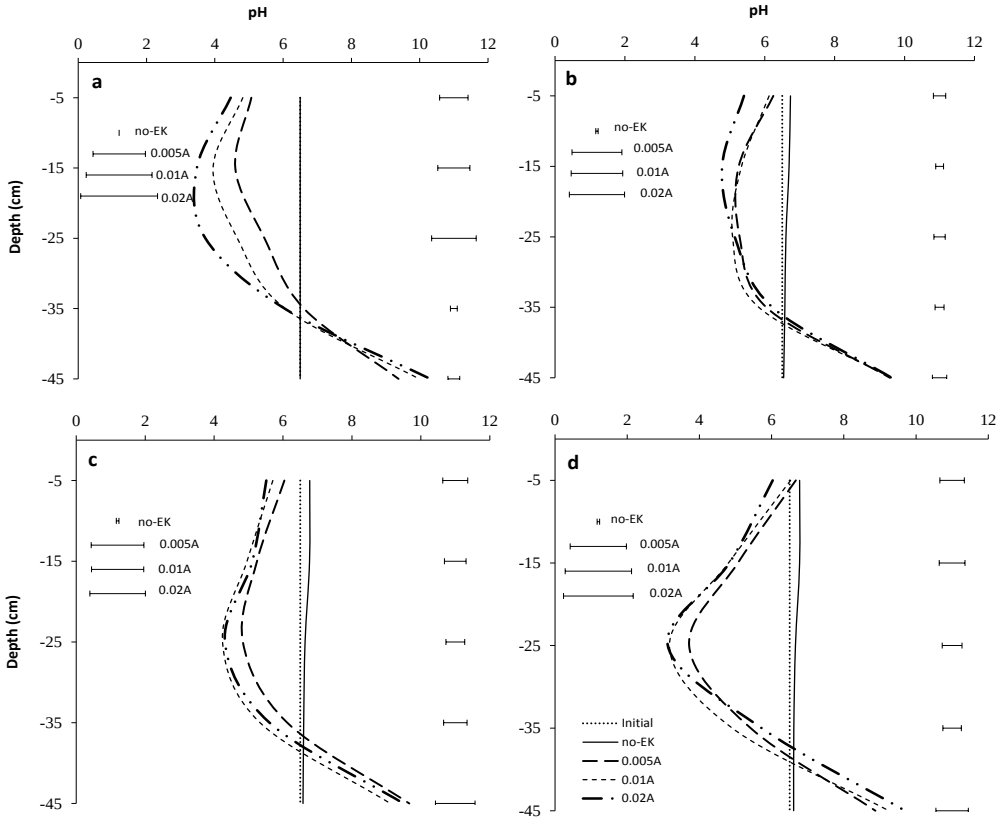

Figure 5-13: pH after application of EK for 24 h on columns irrigated for 9 h with: (a) 0, (b) 10, (c) 20 and (d) 30 mL h^{-1}. Bars at the right of graph are LSD (α=0.05) comparing results between treatments at each depth. Bars at the left of graph are LSD (α=0.05) to compare within treatments

5.4 Discussion

5.4.1 Effect of EK application rate on nitrate movement

The application of EK was found to significantly affect nitrate movement and concentrations in the sand columns. Nitrate movement was also influenced by both the duration and power of EK applied. Figure 5-1 illustrates that a significant change in nitrate concentration was apparent after 9 hours, with concentration differences continuing to increase throughout the 24 hours of EK application. In the first trial, the highest measured nitrate concentration was extracted from 15 cm depth (7 cm below the anode) after the application of 0.02A for 24 h (Figure 5-1). These findings are consistent with Jia et al. (2006) who found that the highest nitrate concentration was measured 2.5 to 7.5 cm from the anode when the electrical current was applied for 6 h. These results confirm nitrate migration to the oppositely charged electrode, with a rise in nitrate concentration near the anode and the lowest concentration found near the cathode.

The application of irrigation to the columns substantially reduced the nitrate concentration in the shallow (5-15 cm) column layers (Figures 5-4 to 5-6). In general, the more water applied, the greater the downwards nitrate movement within the column. This is due to the movement of the nitrate with the gravitational water movement. Not surprisingly, similar results in terms of nitrate distribution were found

in both the EK and control (no-EK) treatments as both were affected by gravitational water movement when irrigation was applied. However, where the irrigation was stopped after 9 h and the EK applied for a further 15 h (Figure 5-6), a greater nitrate concentration was observed at depths <35 cm than was found after applying both EK and irrigation for only 9 h. This increase in nitrate concentration occurred post-irrigation as nitrate moved towards the anode due to electro-migration and diffusion. Similar results were found by Cairo et al. (1996) who found that nitrate ions in a saturated soil moved from the anode towards the cathode with gravitational water movement but when the soil was not saturated (reduced gravitational water movement) and EK was applied, the nitrate migrated toward the anode.

Salt movement (EC) in the sand column was affected by both the irrigation and EK applications. The application of EK was found to increase the EC in the surface (5-25 cm) and decrease EC at 45 cm (Figure 5-2). The increase was due to the negative ions moving upwards towards the anode while at the same time the water within the column was moving downwards from the anode to the cathode under the effect of gravity and electro-osmosis. Consequentially, water accumulated in the bottom of column producing a higher water content and a lower salt concentration through dilution. The effect was greater with increasing EK application rate. These results are consistent with Gibbs and Mitchell (1958) who also found that the rate of solute movement increased when the electrical potential was increased.

As expected, applying good quality (low EC) irrigation water flushed salt from the surface (5-15 cm) layers into the sub-surface (25-35 cm) layers (Figures 5-10 and 5-11). The salt movement was directly related to the rate and duration of water addition with the downwards gravitational water movement generally having a greater ability to move salt ions than the electrical effect achieved by the application of EK.

The pH within the column was affected by both EK and the irrigation applications. Increasing the duration and power of EK applied resulted in an increase in the amount of H^+ and OH^- generated near the anode and the cathode, respectively (Figure 5-3). However, the application of the irrigation water was found to buffer the pH in the surface (5-15 cm) layers and flush H^+ ions downwards in the sand column (Figures 5-11 and 5-12). This suggests that irrigation (and gravitational water movement) has a much greater effect on pH distribution than EK application.

The H^+ (acidic) front was found to migrate faster through the sand column than the OH^- (basic) front (Figure 5-13). This difference occurs as the acidic fronts migrates towards the cathode due to a combination of electro-migration, electro-osmosis, gravity and diffusion, while the basic front migrates from the cathode to the anode (opposite the gravity) due to only electro-migration and diffusion.

5.4.2 Implications for the management of nitrate in irrigated root zones using EK

This work suggests that it should be possible to identify optimal combinations of EK and irrigation management practices to manage the nitrate, salt and pH conditions within a root zone. This would be of benefit in reducing nitrate losses from irrigated root zones.

This study has found that applying EK within a sand column led to an increase in nitrate concentration in the surface layers near the anode (Figure 5-1), which is consistent with results demonstrated in the literature (Eid et al. 2000; Jia et al. 2005). However, the application of EK resulted in negative impacts on the EC and pH within

the column. When irrigation water was applied, the EC in the column was reduced and the pH was buffered towards more benign conditions. However, the nitrate concentration decreased in the surface of the columns with the effect increasing with increasing rate and duration of irrigation.

Under irrigation, nitrate was found to move from the top of the columns due to the influence of gravitational water movement. This downwards nitrate movement due to irrigation application was much greater than the rate of nitrate migration towards the anode achieved by EK. Hence, there seems little benefit in applying EK during irrigation. Rather, EK may be more effective if applied for longer durations either pre- or post-irrigation in an effort to move the nitrate upwards in the column. This would allow nitrate to re-concentrate in the target root zone by migration and diffusion transport processes. For example, in this work 300 mg of nitrate was present in the 0-25 cm layer after the application of 15 h EK following 9 h of 30 mL h^{-1} irrigation (Figure 5-7) compared to 150 mg for the control (no-EK) treatment.

The EC generally increased in the 0-25 cm layers when EK was applied with irrigation. However, increasing the salt concentration in the soil solution above plant specific thresholds has a negative impact on plant growth and yield (Al-Ghobari 2011; Asgari et al. 2012; Ayers & Westcot 1985; Katerji et al. 2003). From the irrigation results, it is clear that the salt concentration was reduced within the 0-25 cm depth where irrigation with rain-water was applied for 9 hours. Thus, the salinity of the soil solution can be controlled by irrigation rate and duration in the presence of EK using good quality irrigation water. The trends observed for EC and nitrate were similar under irrigation, which may suggest that the use of saline irrigation water could result in a salt bulge within the nitrate retention zone because chloride anions will move with nitrate under the influence of EK. Therefore, it seems likely that good quality irrigation water may be required to manage the EC within the root zone. However, further research is required to evaluate the effect of EK on ion movement when saline (and/or sodic) irrigation water is applied.

The pH was influenced by both EK and irrigation practices. In the absence of irrigation, an acidic zone was observed near the anode with the extent increasing with EK power. Additionally, an alkaline (pH ~ 10) zone close to the cathode was observed when no irrigation was applied. However, a pH of ~6 was maintained throughout the column when good quality (pH 7) irrigation water was applied. However, continuing EK post-irrigation resulted in a pH that was acidic at ~25 cm depth after 24 h and was likely affected by poste irrigation drainage. The size of the zone of acidity appeared to be a function of the prior irrigation rate. A reduction in the root zone solution pH to less than 6 may have a negative impact on the availability of nutrients and affect plant growth (Bauder et al. 2011). Therefore, to make the root zone suitable for plant growth and yield, the pH should be maintained at the moderate value. In the surface layers, this may be achieved by using a combination of irrigation and EK (Figures 5-11 to 5-13).

A high alkalinity (i.e. pH ~10) was observed near the cathode during periods when EK was applied and no irrigation was applied (i.e. compare Figures 5-11 and 5-12 to Figure 5-13). This suggests that it may be possible to adequately mitigate the alkalinity effect near the cathode using irrigation applications but if EK needs to be applied for longer durations then consideration should be given to locating the cathode outside of the active root zone to minimise the impact of this alkaline zone on plant growth.

5.5 Conclusion

This chapter has found that EK and irrigation applications can be used to manage the concentration and distribution of nitrate in the root zone. In general, EK can be used

to hold or move nitrate in the zone between the electrodes (i.e. in the 5 to 35 cm column layer in this trial) with increasing EK power and duration increasing the effect. However, the application of EK (particularly at higher rates of application and longer durations) may also result in EC and pH conditions within the root zone which are not conducive to plant growth. The application of irrigation water was found to flush salts from the surface column layers and to buffer the pH changes but was also found to move nitrate downwards and potentially out of the column. This suggests that a combination of irrigation and EK management practices could be used to reduce nitrate losses while managing salt concentrations within a root zone.

Optimal root zone conditions for plant growth involve the maintenance of adequate root zone nitrate, low salt concentrations and benign pH conditions. The optimal combination of EK and irrigation management practice will be a function of the target root zone requirements for the crop being grown, starting root zone nutrient and salt conditions, physical and chemical properties of the soil, and the quality of the irrigation water applied. As the good quality irrigation water applied in this work had a low EC, there is a need for further research to evaluate the impact of using EK to manage sodium and nitrate when saline-sodic irrigation water is applied.

The interaction between these soil, water and EK variables and processes is complex. This work has involved a preliminary evaluation of these interactions by looking at the ion movement when good quality irrigation water and EK were applied at the same time and EK was then continued for a period. However, additional research is required to better understand the interactions between EK and irrigation when these management practices are applied over a series of sequences as would be expected under commercial conditions.

Chapter 6: Using electro-kinesis to manage sodium and nitrate movement in a sand column irrigated with saline-sodic water

6.1 Introduction

Saline-sodic water is recently being used for irrigation purposes in many arid and semiarid areas of the world (Chapter 1). The ability of electro-kinesis (EK) to remove excess sodium (Na^+) and other salts from a sand column was demonstrated in Chapter 4 and subsequent research (Chapter 5) showed that nitrate movement can also be managed within the zone between the electrodes by applying EK. Chapter 5 also demonstrated that nitrate movement, salt distribution and pH between the electrodes were significantly influenced by duration and rate of EK application and irrigation management. However, this study used good quality (low salt) irrigation water and further research is required to evaluate the effectiveness of EK for controlling salt and nitrate movement when saline-sodic irrigation water is applied.

In the previous studies (Chapters 4 and 5), either sodium chloride or a nitrate solution were used to prepare the sand column prior to EK application. In each of these studies the soil solution electrical conductivity (EC) was found to increase between the electrodes with increasing period of EK application. However, a solution EC greater than the plant specific salinity threshold will affect crop growth and productivity (Jungklang et al. 2003; Maas, E. & Hoffman, G. 1977). Thus, to minimise the impacts of salinity on plant growth, the EC within the root zone should be maintained below the threshold level for plant impacts.

This chapter evaluates the effect of EK application on ion movement when saline-sodic irrigation water is applied in the presence of nitrate. The specific objectives are to: (a) confirm the potential to beneficially manage sodium and nitrate movement in a sand column irrigated with saline-sodic water by applying EK, and (b) evaluate a strategy for managing ion movement and maintaining ionic concentrations in the root zone at levels suitable for plant growth using sequential applications of EK, irrigation and fertigation.

6.2 Methodology

Two separate experiments were undertaken in this trial. The first experiment evaluated the effect of EK application on EC and nitrate concentration where the salt and nitrate were initially uniformly distributed within the sand column and no irrigation water was applied to the column. The second experiment evaluated the effect of sequential applications of EK, saline-sodic irrigation water and fertigation with saline-sodic water on the EC and nitrate concentrations in the zone between the electrodes. The sequential management practices adopted in the second experiment were based on the results from chapters 4 and 5 and selected to evaluate the ability to maintain soil ionic conditions (including EC and pH) within reasonable plant tolerances.

Sand columns (50 cm length) were prepared as outlined in Chapter 3.2 to obtain a 12% gravimetric moisture content using saline-sodic water (EC=2 dS m^{-1}, SAR=10) (Table 6-1) with 32 mg L^{-1} nitrate made using calcium nitrate tetra hydrate ($Ca(NO_3)_2.4H_2O$). Suction tubes (Chapter 3.2) were placed in the middle of the sand column to enable extraction of soil solution samples from 5, 15, 25, 35 and 45 cm depth within the columns.

Table 6-1: Saline-sodic solution

Water quality	Target		Measured	Mass (mg)	
	SAR	EC (dS m^{-1})	EC (dS m^{-1})	$CaCl_2.2H_2O$	NaCl
Saline-sodic water	10	2	2 ± 0.02	688	896

In the first experiment, 0.01A EK was continuously applied for 24 hours (using equipment outlined in Section 3.4) and no irrigation water was applied to the column. Soil-solution samples were extracted after 3, 6, 12 and 24 hours to enable measurement of EC and pH as well as the sodium (Na^+) and (NO_3^-) concentrations using the methods outlined in Section 3.5.

In the second experiment, a sequence of EK, EK plus irrigation, drainage and fertigation management practices were applied (Table 6-1). The EK treatment was applied at 0.01A. The saline-sodic irrigation water (EC=2 dS m^{-1}, SAR=10) was prepared using the method described in Section 3.3. For the fertigation application, 32 mg L^{-1} of calcium nitrate tetra hydrate ($Ca(NO_3)_2.4H_2O$) was added to the saline-sodic irrigation water. Both the irrigation and fertigation treatments involved drip application (20 mL h^{-1}) applied to the surface of the sand columns (as per Section 3.3).

Table 6-2: The treatment schedule applied to the sand column over a 48 hour period

Elapsed time (h)	*Treatments*	*Code*
0-6	First period of applying EK	$T_{EK,1}$
6-12	First period of irrigation with saline-sodic water + applying EK	$T_{I+EK,1}$
12-18	First period of no-irrigation and no-EK treatments	$T_{0,1}$
18-24	First period of fertigation	$T_{f,1}$
24-30	Second period of applying EK	$T_{EK,2}$
30-36	Second period irrigation with saline-sodic water + applying EK	$T_{I+EK,2}$
36-42	Second period of no-irrigation and no-EK treatments	$T_{0,2}$
42-48	Second period of fertigation	$T_{f,2}$

The statistical analysis of the highly controlled experiments reported in Chapters 4 and 5 showed that the variation between treatment replicates is sufficiently small to suggest that a single replicate is capable of providing useful information. As the sand column system is chemically simple and does not include an exchange phase, the movement of ions and changes in chemical attributes occur in direct relation to applied electrical fields and/or irrigation. Additionally, the physicochemical effect on sodium and nitrate movement, and relation to pH and EC, in the presence of EK and irrigation was thoroughly statistically investigated in the previous experimental chapters. Hence, as the purpose of this chapter was to demonstrate the ability to adequately suppress non-ideal plant growth conditions only a single replicate of each treatment was used.

6.3 Results

6.3.1 Simultaneous movement of nitrate and sodium using EK

The application of EK produced substantial changes in nitrate concentration, sodium concentration, pH and EC throughout the sand columns (Figures 6-1 to 6-4). In general, the longer the duration of EK application, the greater the movement of ions and differences in ion concentrations. For example, there were only small differences in solution chemical properties after 3 hours of EK application but substantial

differences were generally observed for each property when measured after 12 or 24 hours of EK application (Figures 6-1 to 6-4).

Nitrate was generally moved upwards towards the anode by EK application. Increases in nitrate concentration (after 12 and 24 h) were observed at 15-25 cm (near the anode) while a reduction was observed at 35-45 cm depth (near the cathode) for all EK application periods. The highest nitrate concentration (48 mg L^{-1}) was found at 15 cm depth while the lowest concentration (7 mg L^{-1}) was observed at 45 cm depth when EK was applied for 24 h.

Sodium was generally found to move downwards (towards the cathode) in the sand column due to the EK application (Figure 6-2). Changes in sodium concentration were apparent after 6 hours EK application with small increases observed at 35 cm (near the cathode) and decreases at 5–25 cm. The changes in sodium concentration increased with increase of the application period, but over the 24 hours EK application represented a <16% deviation (<50 mg L^{-1}) from the initial concentrations (300 mg L^{-1}). The maximum sodium concentration (326 mg L^{-1}) was measured at 35 cm depth while the lowest concentration (256 mg L^{-1}) was found at 15 cm depth after 24 hours of EK application.

Substantial changes in EC were observed through the sand column due to EK application (Figure 6-3). A large increase in EC was observed at 15 cm depth and a smaller increase at 5 cm (near the anode). However, there was little difference in EC at both 25 and 35 cm depth but the EC was decreased substantially by EK application at 45 cm depth (near the cathode). For example, the EC at 15, 35 and 45 cm depth after 24 hours of EK application were 3.8, 2.3 and 0.93 dS m^{-1}, respectively.

The EK application resulted in a substantial decrease in pH at 15 cm depth and a substantial increase at 45 cm (near the cathode) (Figure 6-4). At 15 cm, the pH became intolerably acidic (~4) while at 45 cm depth the pH became excessively alkaline (~10) for the majority of agricultural applications.

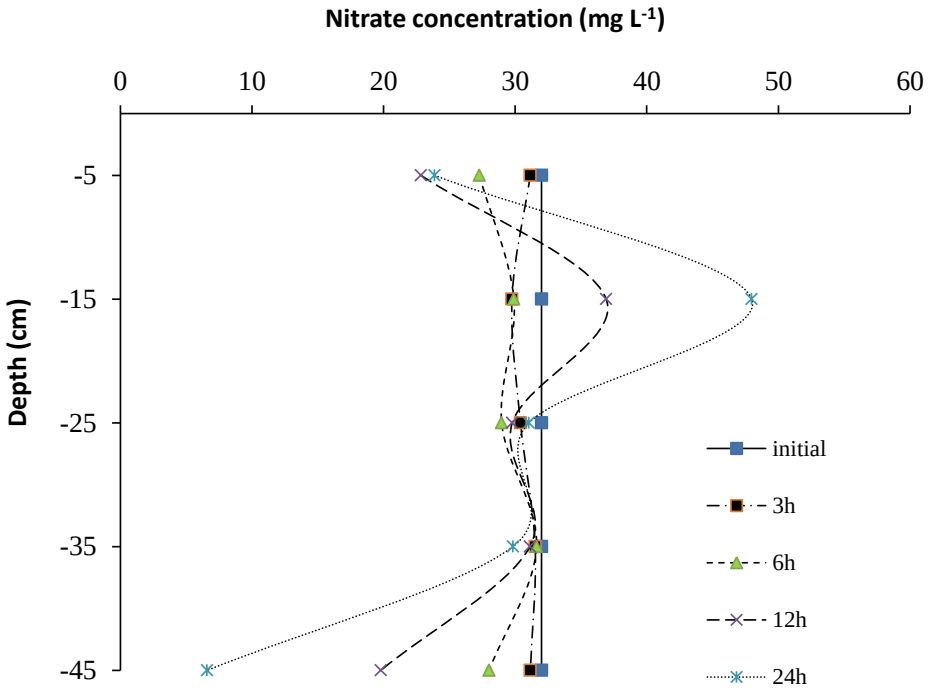

Figure 6-1: The effect of applying 0.01A EK on nitrate concentration in a sand column

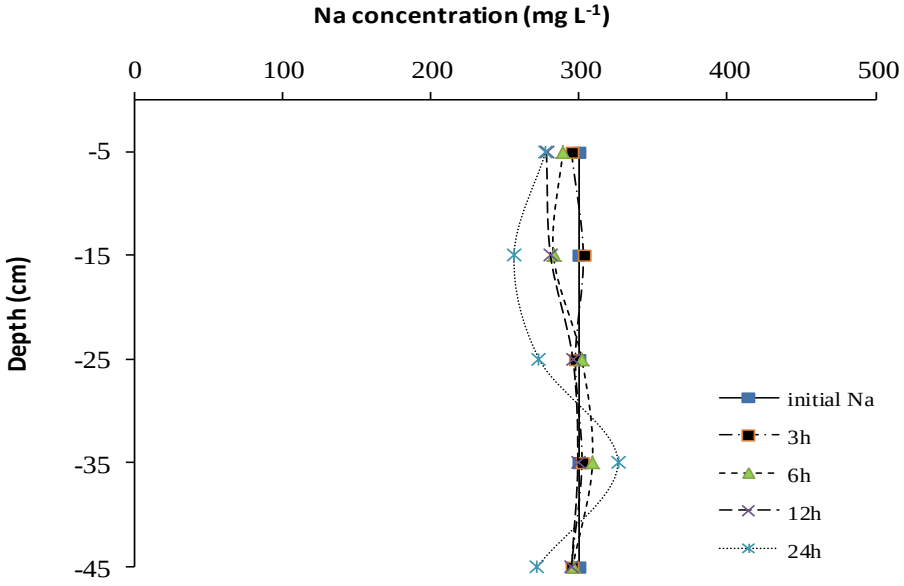

Figure 6-2: The effect of applying 0.01A EK on sodium concentration in a sand column.

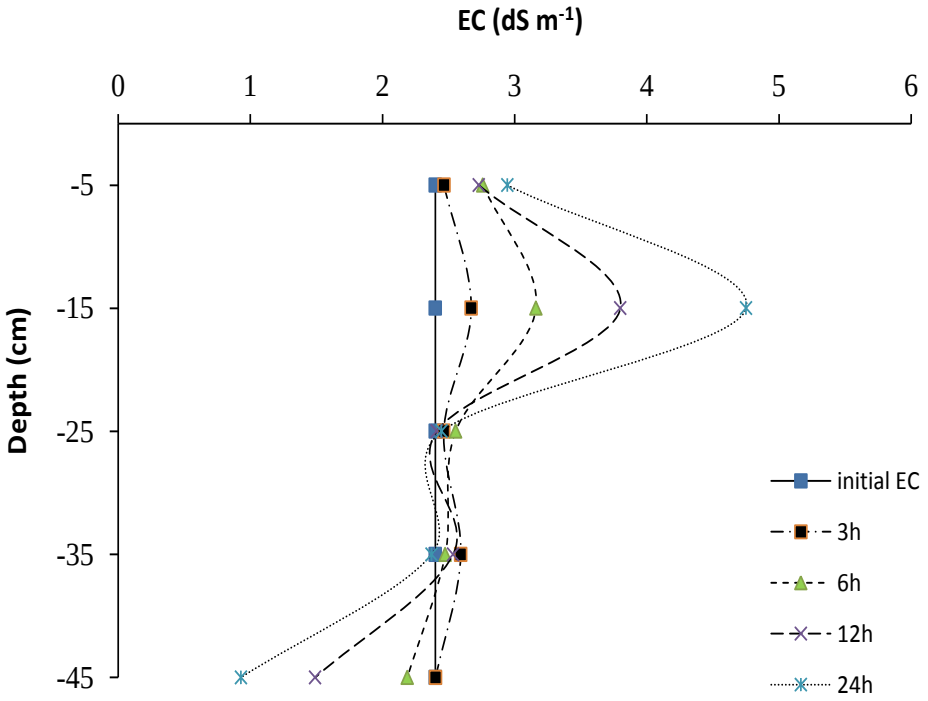

Figure 6-3: The effect of applying 0.01A EK on electrical conductivity in a sand column.

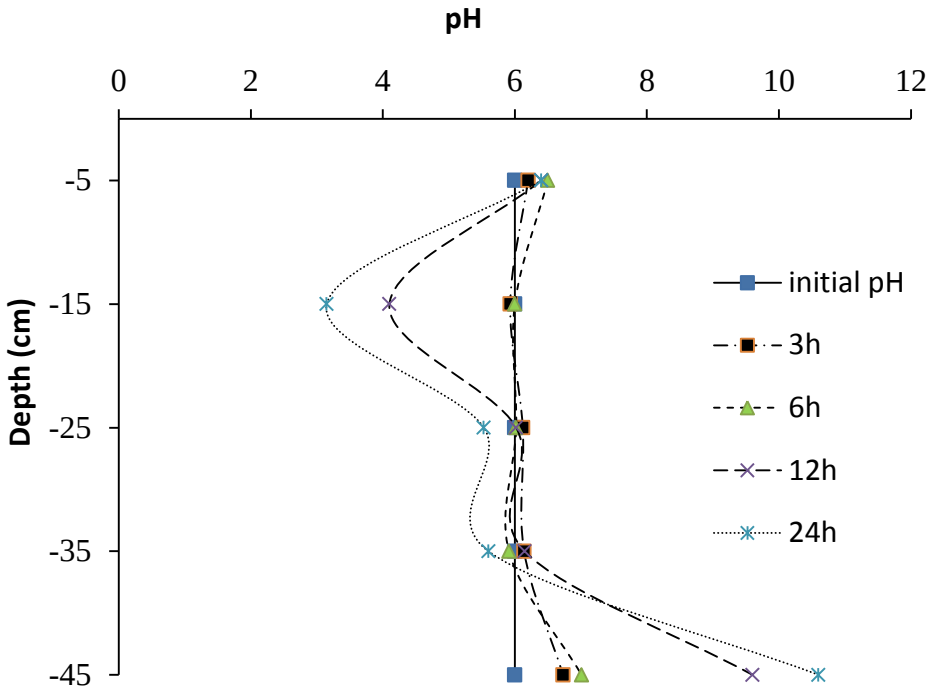

Figure 6-4: The effect of applying 0.01A EK on soil solution pH in a sand column.

6.3.2 Movement of nitrate and sodium with sequential EK, irrigation and fertigation applications

The sequential application of EK, irrigation and fertigation produced dynamic fluctuations in the concentration of ions within the sand column (Figures 6-5 to 6-8). The application of irrigation generally leached nitrate from the surface (5 and 15 cm) layers while EK and fertigation applications increased the nitrate concentration in these layers (Figure 6-5). However, the effect of irrigation application was dominant with the concentration decreasing (from 32 mg L^{-1} initially) to 19 and 18 mg L^{-1} at 5 and 15 cm, respectively after the first irrigation application (i.e. 12 hours total treatment). By comparison, the EK applications resulted in small increases in nitrate concentration in the surface layers and similarly small decreases in concentration at 25 and 35 cm depth. Turning off the electrical power allowed drainage and diffusion to involve for transporting ions within the column under the effect of gravity and a concentration gradient, respectively. As expected, fertigation increased the nitrate concentration most notably in the surface layers but also throughout the column. The highest nitrate concentration (42 mg L^{-1}) was recorded at 35 cm depth after one management cycle (24 hours) but the concentration at this depth then decreased to ~24 mg L^{-1} by the end of the second management cycle. The nitrate concentration at 45 cm did not vary greatly from the initial concentration throughout the management sequences.

The fluctuations in sodium concentration within the sand column (Figure 6-6) were generally smaller than those observed for nitrate (Figure 6-5). In general, the application of irrigation and fertigation (which used saline-sodic water) both increased the sodium concentrations while the EK and drainage phases tended to decrease sodium concentrations. The highest sodium concentration of 358 mg L^{-1} was observed at 35 cm depth after the application of the second application of saline-sodic irrigation water. The lowest concentration of 237 mg L^{-1} was observed at 15 cm depth at the end of the second application of EK (ie. 30 hours).

The EC within the sand column fluctuated between 2 and 3 dS m^{-1} throughout the management cycles (Figure 6-7). Oscillations in salinity were primarily associated with irrigation, whether coupled with EK or fertigation. The EC at 5 and 15 cm depth increased with the initial EK and irrigation applications (ie. <12 hours) while the EC at 35 and 45 cm depth did not vary greatly during these initial treatments. However, the EC at 35 cm depth increased rapidly during the first fertigation application (i.e. 18-24 hours) and at 45 cm during the second drainage and fertigation periods (i.e. 36-48 hours).

The pH within the sand column stayed between 5.5 and 7 during the first 30 hours of the management sequence (Figure 6-8). However, the second application of EK and irrigation (i.e. 36 hours) resulted in the pH at 15 cm depth decreasing to ~4.8 and then ~4.0 after the subsequent drainage and fertigation cycles (i.e. 48 hours).

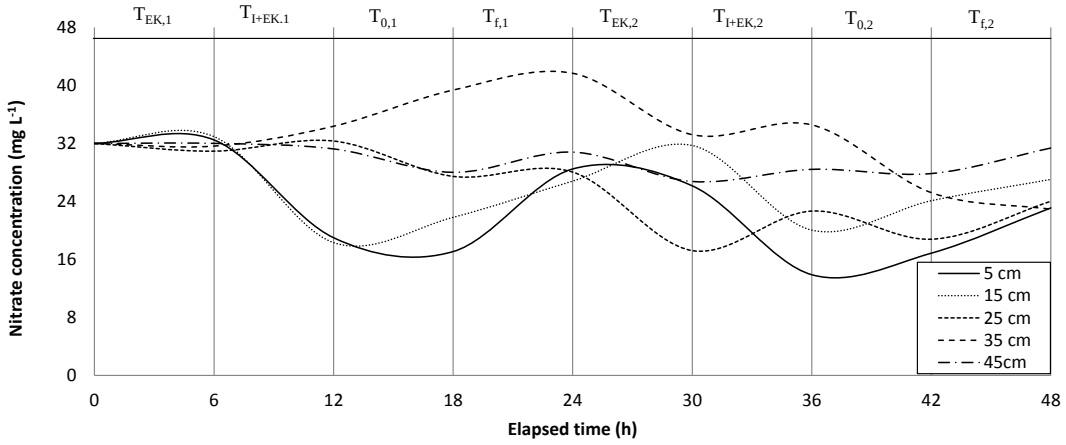

Figure 6-5: Variation in nitrate concentration within a sand column with sequential applications of EK, irrigation and fertigation treatments.

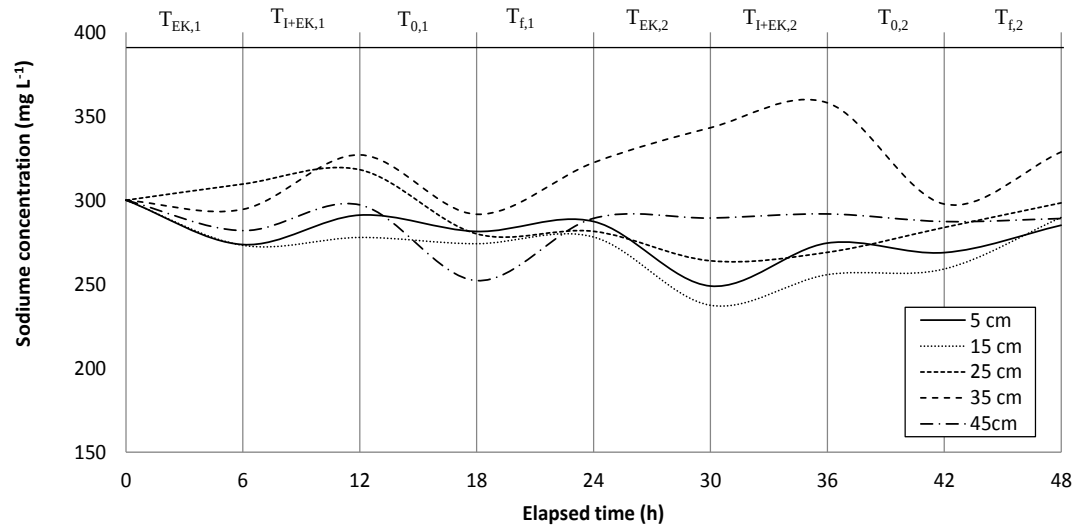

Figure 6-6: Variation in sodium concentration within a sand column with sequential applications of EK, irrigation and fertigation treatments

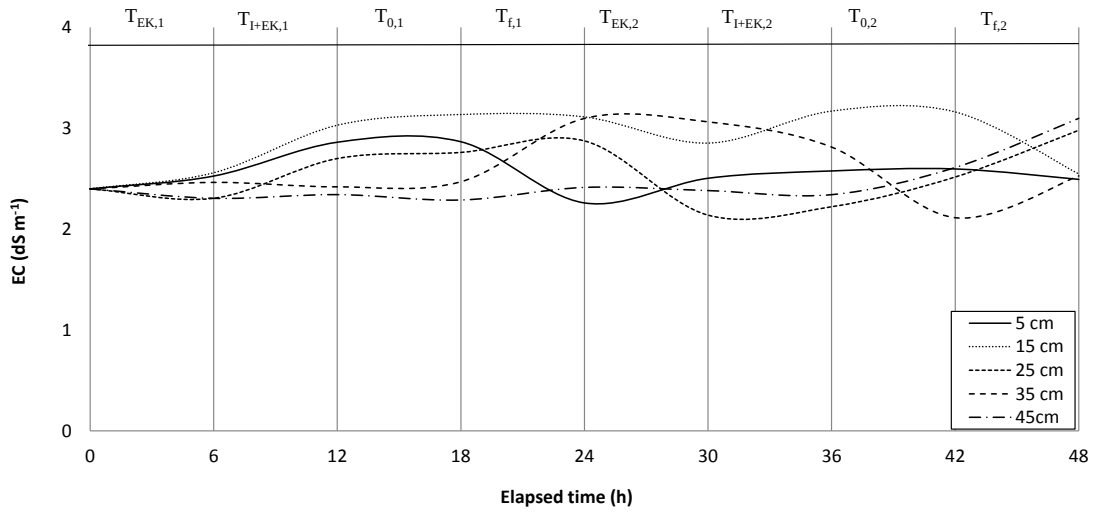

Figure 6-7: Variation in EC within a sand column with sequential applications of EK, irrigation and fertigation treatments.

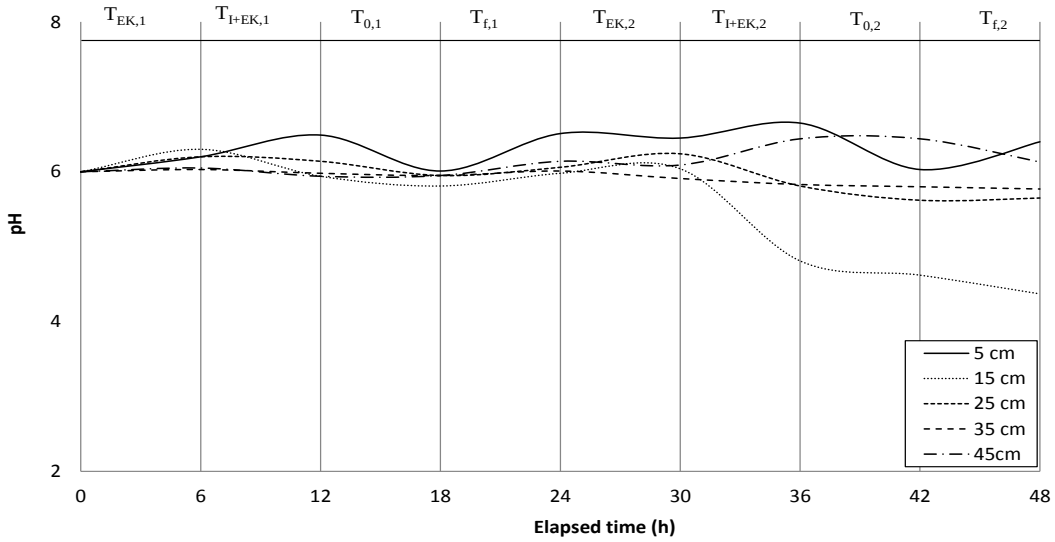

Figure 6-8: Variation in pH within a sand column with sequential applications of EK, irrigation and fertigation treatments.

6.4 Discussion

6.4.1 Using EK to simultaneously maintain nitrate and remove sodium from saline-sodic root zones

The ability to use EK to simultaneously move nitrate and sodium ions in opposite directions in a sand column has been demonstrated (Figures 6-1 and 6-2). The nitrate was shown to move upwards towards the anode while the sodium moved downwards towards the cathode. This movement is consistent with the theory of electro-migration

(Chapter 2.6) due to the application of EK and suggests that EK could be used for managing nitrate and sodium movement in agricultural applications.

The increase in nitrate concentrations observed at 5-25 cm depth in the sand column (Figure 6-1) is consistent with the observations of Jia et al. (2006) and suggests that the effect of electro-migration (i.e. movement of the charged ions) on movement is greater than the effect of electro-osmosis (i.e. movement downwards due to bulk water flow under the influence of the electric field). Sodium ions migrated toward the cathode due to both electro-migration and electro-osmosis processes (Eid et al. 2000) resulting in the higher sodium concentration observed at 35 cm depth (Figure 6-2). It also seems likely that the lower concentration of sodium at 45 cm depth is due to leaching of the sodium at this depth from the sand column because of the increased water drainage associated with electro-osmosis.

Applying EK has been shown (Chapters 4 and 5) to greatly affect salt distribution in a sand column. In this work, an increase in salt concentration was found at 0-25 cm when EK was applied with the effect increasing with EK application time (Figure 6-3). The rise in EC is due to increased accumulation of negative ions proximal to the anode zone, further enhanced by a decrease in soil moisture content. However, EC was observed to slightly increase at 35 cm, which is likely a result of convection processes (Wagenet 1983). The EC was observed to decrease at the cathode because this is the "washed" electrode with bulk downwards water movement moving the salts below this depth and out of the column in the drainage water.

The changes in pH observed near the electrodes are consistent with the effects observed in the earlier work (Chapters 4 and 5) with the effect increasing with period of EK application. In this work, the acidic front is shown (Figure 6.4) to move towards the cathode at a rate that is higher than the movement of the basic front towards the anode. This difference is because the acidic front (H^+) moves downwards in this case under the combined influence of electro-migration, electro-osmosis, gravity and diffusion, while the basic front (OH^-) moves upwards from the cathode to the anode due to only the effect of electro-migration and diffusion.

6.4.2 The effect of sequential EK, irrigation and fertigation applications on nitrate and sodium movement

The sequential application of EK, irrigation and fertigation (Figures 6-5 to 6-8) has been shown to be an effective strategy for managing the movement of nitrate and sodium within a sand column. In general, nitrate was shown to move upwards, and sodium downwards, in the column during periods of EK while the periods of irrigation flushed nitrate downwards. The irrigation treatment applied sodic water to the surface of the column while the fertigation treatment involved the application of water containing both sodium and nitrate to the column surface. The periods of drainage enabled redistribution within the column by both diffusion and hydraulic movement under gravity. Hence, this combination of treatments resulted in a highly dynamic system with fluctuations in ion concentrations at specific depths reflecting the time-lag associated with the various moving ionic and hydraulic fronts within the column.

The management regime applied was found to reduce the sodium concentration in the 5-25 cm depths with these ions being moved downwards during application of both EK and irrigation/fertigation treatments. The sodium accumulated at 35-45 cm depth (Figure 6-6) and was likely leached from the column. By contrast, the nitrate was

generally moved upwards by electro-migration during EK application but the effect was relatively small compared to the leaching of nitrate associated with the irrigation applications. Hence, while there were fluctuations in response to the application of the different management treatments, a general decline in the nitrate concentration was observed in the surface 5-25 cm depth (Figure 6-6). This suggests that a more optimal management strategy for maintaining nitrate concentrations in the surface layers would require a relatively longer period of EK (or higher EK electrical current rate) or shorter period (and/or smaller application rate) of irrigation. However, given the wide range of potential column design (e.g. length, electrode separation), media (e.g. soil texture, CEC, packing density) and irrigation/fertigation management variables (e.g. water quality, application rate, fertiliser composition and concentration) the optimisation of a combined EK and irrigation system will require the development of a quantitative model which incorporates both the soil-water hydraulic and EK electrical field phenomenon.

A major objective of applying sequential management strategies was to evaluate the ability to maintain the column pH and EC within acceptable ranges while effectively maintaining or increasing the nitrate concentration and decreasing the sodium concentration within the target root zone. While the management strategy adopted in this trial may not be optimal, it has demonstrated that it is possible to achieve this objective. The pH within the column was generally maintained in the range of 5.5 to 6.5 throughout the trial. However, the pH at the 15 cm depth (i.e. near the anode) decreased below this range after the application of the second EK treatment and did not increase with the application of the subsequent management treatments. This decrease in the soil pH may have toxic impact on plants and/or indirectly affect the availability of plant nutrients and toxic elements. Therefore, it suggests that there would be benefit in optimising the relative duration and intensity of the EK application depending on the target root zone requirements.

The EC was maintained in the range of 2 to 3 dS m^{-1} at all depths throughout the trial. These conditions are generally suitable for a range soils and crops. For example, Maas and Hoffman (1977) indicate that the salinity threshold for tomatoes is 2.5 dS m^{-1} while that of cotton is 7.7 dS m^{-1}. The lower EC (i.e. <3 dS m^{-1}) observed with the applied treatments also contrasts with the EC ~5 dS m^{-1} observed when EK was applied without irrigation in the earlier work (Figure 6-3) and demonstrates the beneficial effect of leaching associated with the irrigation and fertigation treatments.

6.5 Conclusion

This chapter has found that EK is effective in simultaneously moving nitrate upwards and sodium ions downwards in saline-sodic sand columns. Hence, EK can be used to assist in the simultaneous management of nutrients and salts within the root zone. However, depending on the design of the system, applying EK by itself may result in zones of pH and EC within the root zone which could be deleterious to plant growth.

The effect of sequentially applying EK, irrigation and fertigation was evaluated in this work. This management regime demonstrated that the pH and EC in the column can be maintained within acceptable limits while still obtaining the nutrient management and sodium leaching benefits of EK application. While nitrate retention and sodium removal benefits were identified using the management regime evaluated, the benefit for nitrate retention would have been greater if longer periods of EK (or higher power applications) where applied or alternatively shorter periods of irrigation (or lower

water application rates) were used. Clearly the dynamic nature of the changes within the sand column and time-lag associated with changes in each column depth due to the sequential application of the management treatments make it difficult to identify optimal strategies. Hence, there is a need to develop a quantitative model that incorporates both soil-water movement and the effect of EK on ion movement. The development of such a model would enable the evaluation of alternative strategies and the identification of optimal EK and irrigation management practices for specific soil and plant conditions.

Chapter 7: Development of a numerical model to predict nitrate and salt movement in soil columns due to electro-kinesis and irrigation applications

7.1 Introduction

The application of electro-kinesis (EK) has been shown to affect the movement of nitrate (Chapter 4) and salts including sodium (Chapter 5) in sand columns. In general, the application of EK moves anions (e.g. nitrate) towards the anode and cations (e.g. sodium) towards the cathode. By locating the anode near the column surface and the cathode near the bottom of the column it is possible to hold and/or move nitrates towards the column surface and migrate sodium downwards in the column. This research (Chapter 4 and 5) suggested that EK may be a useful management technique to improve anionic nutrient retention while also removing cations (including sodium) from saline-sodic root zones. However, depending on the power and duration of EK applied there was also the potential to create areas within the root zone with an extreme pH or electrical conductivity which could be deleterious to plant growth.

Subsequent trials (Chapter 6) evaluated the potential to manage nitrate and sodium movement in a saline-sodic irrigated sand column using a combination of EK, irrigation and fertigation treatments. These trials demonstrated that by using the combination of management practices the pH and EC within the sand column could be maintained within acceptable limits while still obtaining the nutrient management and sodium leaching benefits of the EK application. However, it also showed that the dynamic nature of the concentration changes observed within the column, and time-lag associated with these changes at each column depth, would make it difficult to identify optimal management strategies without the use of a numerical model incorporating both soil-water movement and the effects of EK application on solute transport. As no such model was able to be found, the aim of the work reported in this chapter is to: (a) develop and validate a combined soil-water and EK model, and (b) demonstrate the application of this combined model for understanding ion movement and concentrations in a simple irrigated EK column system.

7.2 Development of the Diffusion Convection Electro-osmosis Electro-migration Model (DCEEM)

This work has developed a combined soil-water, solute movement and EK model to numerically describe soil-water and solute movement under the effect of gravitational and hydraulic potential gradients, concentration gradients, and electrical potential gradients induced by EK application. This "Diffusion Convection Electro-osmosis Electro-migration Model" (DCEEM) captures the major phenomenon influencing ion movement within a one-dimensional soil column.

The DCEEM models soil-water movement using the Richards' equation (Celia et al. 1990) with the water flux driven by both the hydraulic and electric gradients. Solute transport is modelled by solving the transport equation (Yeung & Mitchell 1993), while the electro-migration process is simulated based on Huweg's (2013) one-dimensional model. The soil column is divided into discrete segments and a finite difference method (FDM) is used to solve the partial differential equations (PDEs) within the model.

The model was developed with the assistance of Dr Duc Ngo-Cong (Computational Engineering and Science Research Centre, USQ) who provided advice in relation to computational solutions and coded the model software. The overall structure and operation of the model is shown in Figure 7-1. Additional details on the numerical operation of DCEEM are provided in Appendix 1.

7.2.1 Soil and Electric Parameters used in DCEEM

A range of model parameters describing the solute as well as soil hydraulic and electrical parameters are required to solve the PDEs including: Initial nitrate concentration (C_n), initial electrical conductivity (σ_h), measured speed of the depletion surface, injected current (I), voltage difference between the anode and cathode (V) , effective saturated diffusion coefficient in the soil (D_{eff}), the coefficient of electro-osmosis permeability of soil (K_e), the saturated hydraulic conductivity (K_s), the inverse of the air-entry value and pore-size distribution index (η). Initial values for these parameters were obtained from the literature or calculated from the earlier trials. The soil hydraulic and electric parameters used in the later simulations of the DCEEM model are summarised in Table 7-1.

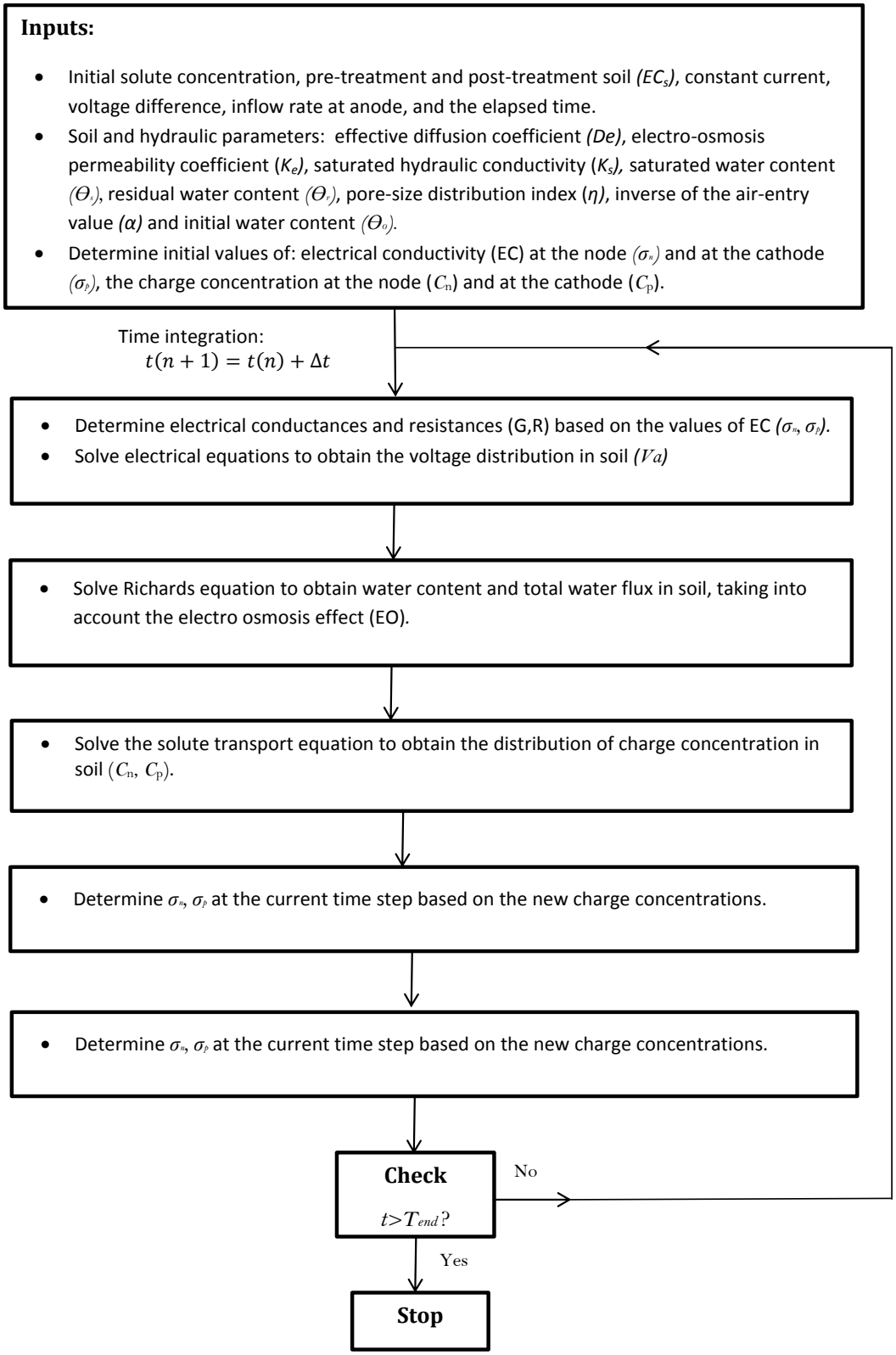

Figure 7-1: Flowchart of DCEEM model

Table 7-1: The DCEEM parameters

Parameter	Abbreviation	Value
Concentration and electric parameters		
Initial nitrate concentration	C_n	1600 mg L^{-1}
Initial electrical conductivity	σ_h	0.27 $S\ m^{-1}$
Measured speed of the depletion surface		2.10^{-6} m s^{-1}
Injected current	I	0.01A
Voltage	V	100 V
Inflow rate	Q_A	0 and 30 mL h^{-1}
Soil and hydraulic parameters		
The effective saturated diffusion coefficient in soil	D_{eff}	$7e^{-8}$ $m^2\ s^{-1}$
The coefficient of electro-osmosis permeability of soil	K_e	$8e^{-9}$ $m^2\ v.\ s^{-1}$
Saturated hydraulic conductivity	K_s	$4.5e^{-2}$ $cm\ s^{-1}$
Initial water content	Θ_o	0.10 $cm^3\ cm^{-3}$
Residual water content	Θ_r	0.01 $cm^3\ cm^{-3}$
Saturated water content	Θ_s	0.43 $cm^3\ cm^{-3}$
Inverse of the air-entry value	α	0.17 cm^{-1}
Pore-size distribution index	η	2.05

7.2.2 Model limitations

Only a preliminary version of the DCEEM model was able to be developed with the time and resources available. While the model was considered adequate for the current study, key limitations of the current version include:

- one-dimensional model,
- fixed physical dimensions (50 cm length and 10 cm diameter) with column mounted vertically and fixed electrode configuration (ie 5 cm anode and 45 cm cathode depth),
- fixed lower boundary condition (zero flux),
- fixed surface boundary condition for irrigation (i.e fixed water application rate), and
- can only be used to evaluate sequential EK and water applications (rather than simultaneous).

It should also be noted that the ion concentration calculated by the model is provided in units of Coulomb m^{-3}. This value was subsequently converted to mg L^{-1} using 96,500 Coulomb per mole of electrons or Ampere-second (Ahmad, (2003).

7.3 Materials and Methods

7.3.1 Model validation experimental design

Several trial treatments were conducted to investigate the effect of water applications and EK on the movement of soil-water and solutes in a closed sand column. Sand columns (50 cm length and 10 cm diameter) were prepared as described in section 3.2. Calcium nitrate tetra hydrate ($Ca(NO_3)_2.4H_2O$) solution was prepared at 1600 mg L^{-1} and was applied to the sand during column construction to produce a uniform volumetric water content of 10%. A plastic container was filled with rain water (EC = 0.016 ± 0.02 dS m^{-1}, pH = 7 ± 0.04) and placed above the vertical sand column to

provide water for drip irrigation using the method described in section 3.3. The bottom of the column was capped to prevent drainage from the column.

Three trial treatments with two replications each were conducted with the data then used to validate the DCEEM model. The trials involved measuring soil-water and solute changes after either gravity (i.e. drainage), EK application or irrigation water application (Table 7-2). In each case the treatment was applied for a total of 6 hours. At the end of treatment application, soil samples were extracted at 5, 15, 25, 35 and 45 cm depth from the columns, oven dried at 105˚C for 24 h and the gravimetric water content and electrical conductivity (EC) measured using the methods described in section 3.5. The DCEEM model was then used to simulate each trial treatment and the coefficient of determination (R^2) calculated as a measure of the difference between the observed and model predicted values.

Table 7-2: Trial conditions used for the model validation, where Trial 1 assessed gravitational effects, Trial 2 assessed the effect of electro-kinesis and Trial 3 evaluated the effect of drip irrigation application

Model parameter	Trial 1	Trial 2	Trial 3
Irrigation application	0	0	30 mL h^{-1}
EK application	0	0.01A	0
Duration	6 h	6 h	6 h

7.3.2 Demonstration of model operation

The validated DCEEM model was used to demonstrate the potential to evaluate EK and irrigation management strategies. Two sets of simulation studies were conducted. In each study, the simulated sand columns were parameterised using the values as shown in Table 7-1 and had an initial uniform EC = 2.7 dS m^{-1}, nitrate concentration = 1600 mg L^{-1} and 10% volumetric water content.

The first study simulated an irrigation application (20 mL h^{-1}, EC = 0 dS m^{-1}, applied for 9 hours) followed by four different periods (3, 4, 5 or 6 h) of 0.01A EK application with the objective of demonstrating the effect of EK application period on nitrate redistribution. The second study simulated a sequence of EK (either 0 A or 0.01A for 9 h) and irrigation (20 mL h^{-1}, EC = 0 dS m^{-1} for 6 h) applications (Figure 7-2) to demonstrate the variations in ion concentration at different column depths throughout a series of management cycles, and enable comparison of solute changes both with and without the addition of EK.

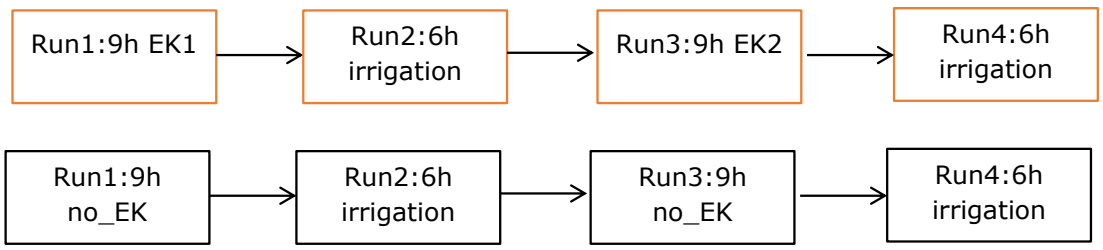

Figure 7-2: Sequence of EK and irrigation management options simulated to demonstrate the DCEEM model capability.

7.4 Results and discussion

7.4.1 Validation of the DCEEM model

7.4.1.1 *Trial 1: Gravitational effect*

The DCEEM model predictions of volumetric water content within the sand column after 6 hours of drainage are consistent with the measured column data (Figure 7-3). A lower water content was observed in the surface layers along with a higher water content towards the base of the column. The predicted volumetric moisture content was generally within 2% of the average measured moisture content and the coefficient of determination (R^2) between the measured and predicted data was 0.79. This confirms that the soil-water component of the model operates appropriately with the model accurately predicting the soil water content at different depths in the sand column under drainage conditions.

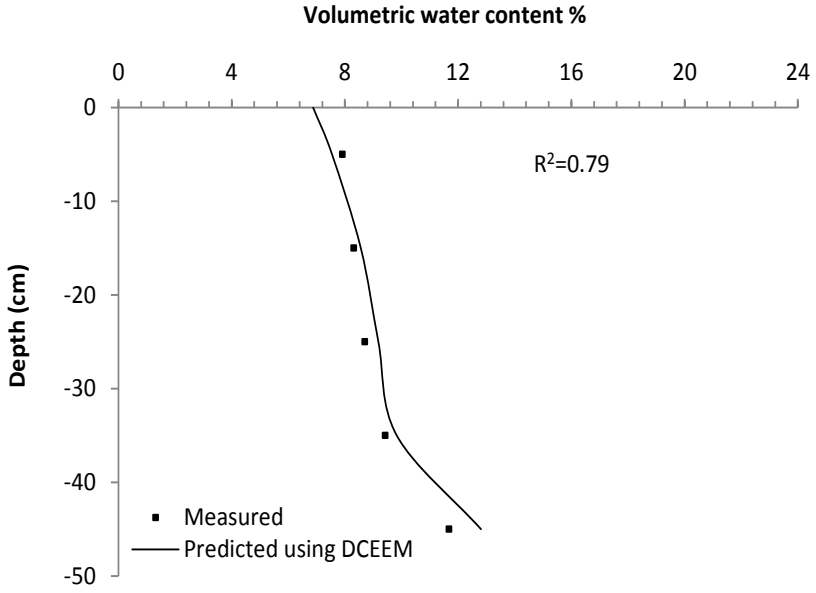

Figure 7-3: The predicted volumetric water content by the DCEEM compared with the measured data after 6 hours of case1

7.4.1.2 *Trial 2: Electro-kinesis effect*

The DCEEM model accurately predicted (R^2 = 0.96) the changes in EC throughout the sand column due to the application of EK (Figure 7-4). The model predicted the pattern of EC variations throughout the column and there were only minor differences (<0.2 dS m^{-1}) between the predicted and average measured EC at all depths. The model also adequately predicted (R^2 = 0.80) the volumetric moisture profile within the column due to EK application (Figure 7-5). While the differences between the predicted and average measured water content were generally small (<2%), there was a slight trend in the model to over-predict the surface moisture content and under-predict the water content towards the bottom of the column.

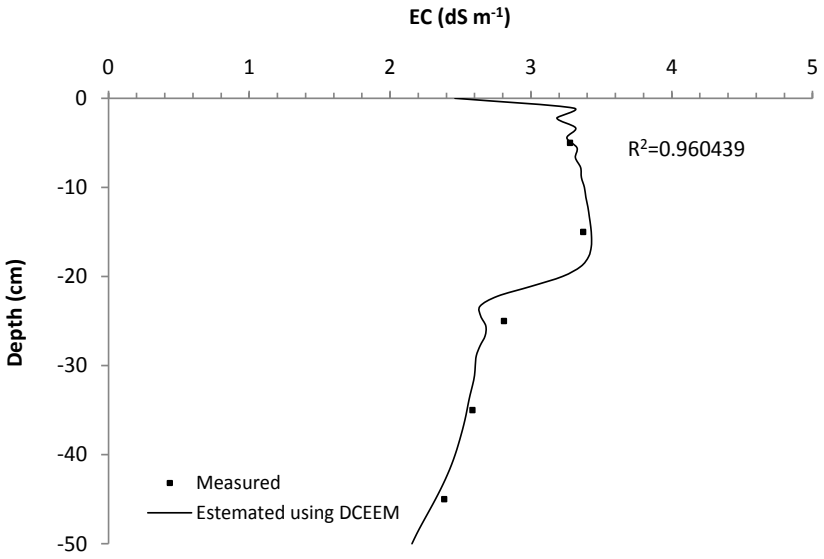

Figure 7-4: The variation in the predicted EC by the DCEEM compared with the measured data after 6 hours of case2.

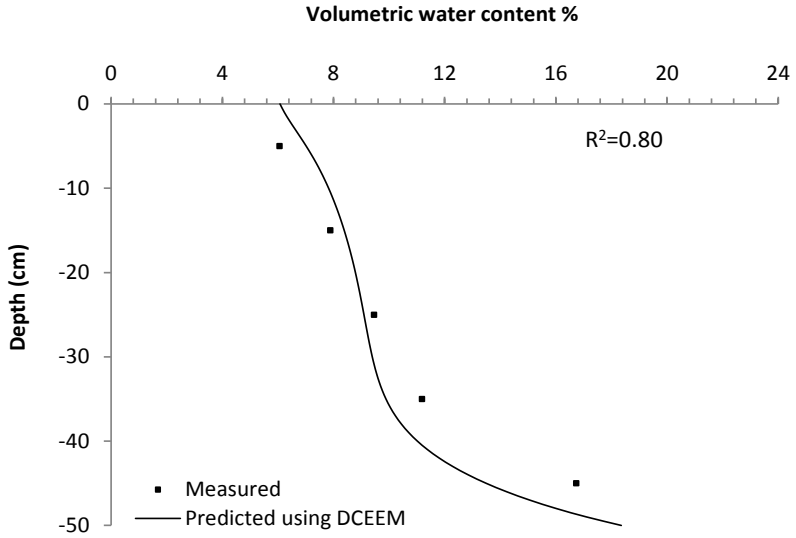

Figure 7-5: The predicted volumetric water content by the DCEEM compared with the measured data after 6 hours of case1

Given that this trend was not observed when the model was used to simulate drainage alone (Figure 7-3), this suggests that the model (with the current parameterisation) may have a slight tendency to underestimate the effect of electro-osmosis on soil-water movement towards the cathode when EK is applied.

7.4.1.3 *Case 3: Irrigation effect*

The DCEEM model accurately predicted (R^2 = 0.92) the change in EC throughout the sand column when the irrigation treatment was applied (Figure 7-6). Both the predicted and measured data have a similar trend, with a lower EC near the surface

and slightly increased EC near the base of the column. The upper portion of the sand column was diluted by the applied irrigation (rain water, EC=0.016 dS m^{-1}) and the downwards movement of the irrigation wetting front drives solutes deeper into the profile (Oster et al. 1984). The volumetric water content throughout the column was also adequately predicted (R^2 = 0.71) by the model (Figure 7-7) with only a small under-prediction of soil-moisture near the bottom of the column. This work confirms that DCEEM can be used to accurately predict the soil-water and solute movement in sand columns during periods of irrigation, drainage or EK application.

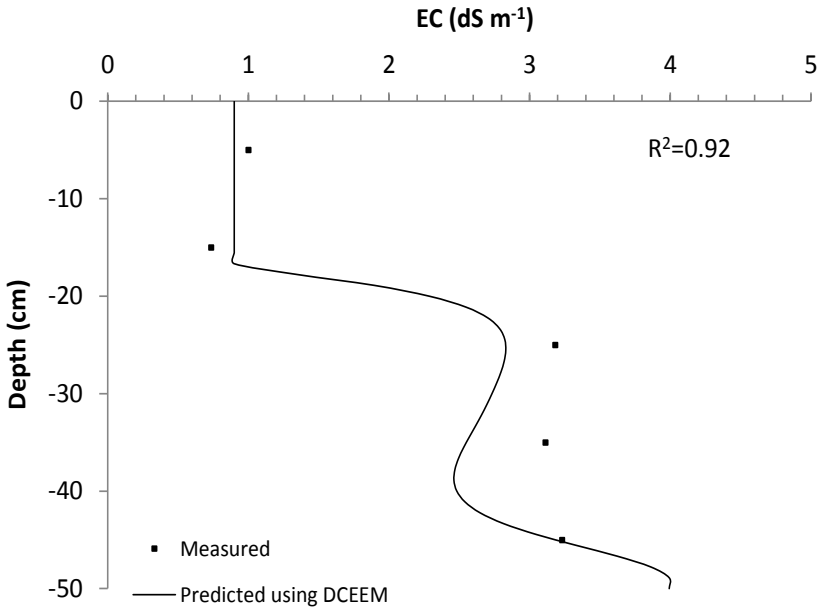

Figure 7-6: The variation in the predicted EC by the DCEEM compared with the measured data after 6 hours of case3

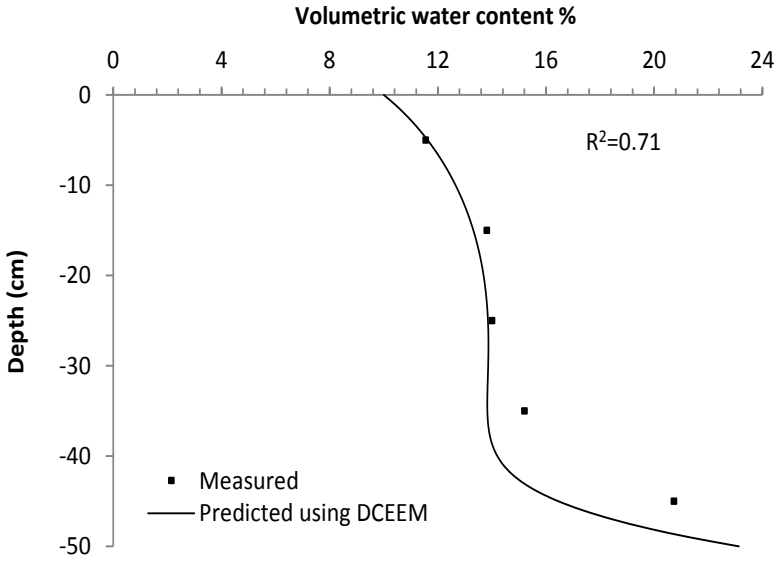

Figure 7-7: The predicted volumetric water content by the DCEEM compared with the measured data after 6 hours of case3.

7.4.2 Using DCEEM to demonstrate the effect of EK and irrigation on nitrate and solute distribution within the sand columns

7.4.2.1 *Effect of EK application period on EC and nitrate re-distribution after irrigation*

The salt distribution predicted after applying irrigation for 9 h (Figure 7-8) shows the effect of convective ion movement from the surface layers towards the base of the column. For example, at 10 cm depth the EC has decreased from the initial value (EC=2.7 dS m^{-1}) to be 1.5 dS m^{-1} after the irrigation application, while at 50 cm the EC has increased from 2.7 to 3.9 dS m^{-1}. However, applying EK after the irrigation was stopped resulted in electro-migration that moved ions upwards from the base of the column. This is consistent with the effect demonstrated by Mattson et al. (2002) and produced a decrease in EC at 50 cm and an increase in EC in the 20-40 cm layers. The effect was shown to increase with increasing period of EK application (Figure 7-9) and consistent with the findings of Cho (2009).

Nitrate movement was also shown to be greatly affected by irrigation (Figure 7-10) with reductions in nitrate concentration at the surface (0–10 cm) and an increase at the base (50 cm). For the simulated case, the nitrate concentration at 10 cm was reduced from the initial (1600 mg L^{-1}) value to ~26 mg L^{-1} but was increased at 50 cm to ~1990 mg L^{-1} by the irrigation application. Such a result was expected as nitrates move readily with water flux (Lamb et al. 1985; Martinez & Guiraud 1990; Meisinger et al. 1991; Powlson 1988; Wellings & Bell 1980). However, applying EK after the irrigation treatment resulted in a progressive redistribution of the nitrate upwards towards the anode within the profile (Figure 7-11) with the increase in nitrate at 20-30 cm depth greatly influenced by increasing the period of EK application. However, the increase in nitrate concentration was accompanied by an increase in EC and the identification of an optimal EK management strategy would also need to consider the relevant crop salinity thresholds.

The application of irrigation increased the soil-water content throughout the column (Figure 7-12) while the subsequent application of EK (Figure 7-13) resulted in the movement of water downwards in the column through electro-osmosis. However, the main effect of EK application on soil-water movement seems to occur relatively quickly with the model predicting the majority of changes within 3 h of EK application and only minor changes in soil-water content thereafter with increasing EK application period.

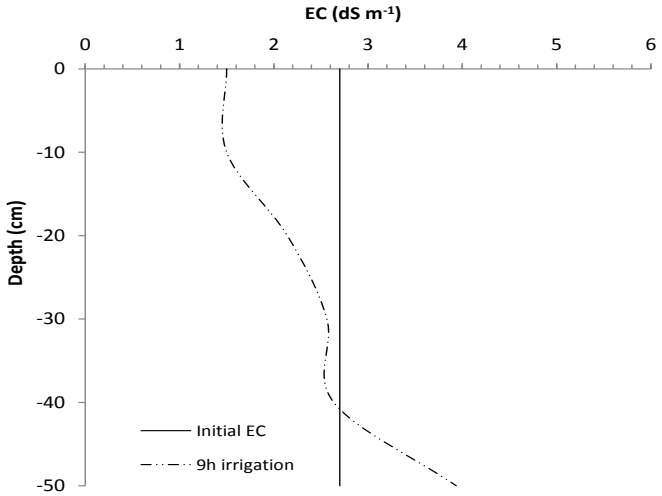

Figure 7-8: The predicted EC with depth from running the DCEEM model to simulate applying 9 h irrigation at rate of 20 mL h^{-1} without applying EK

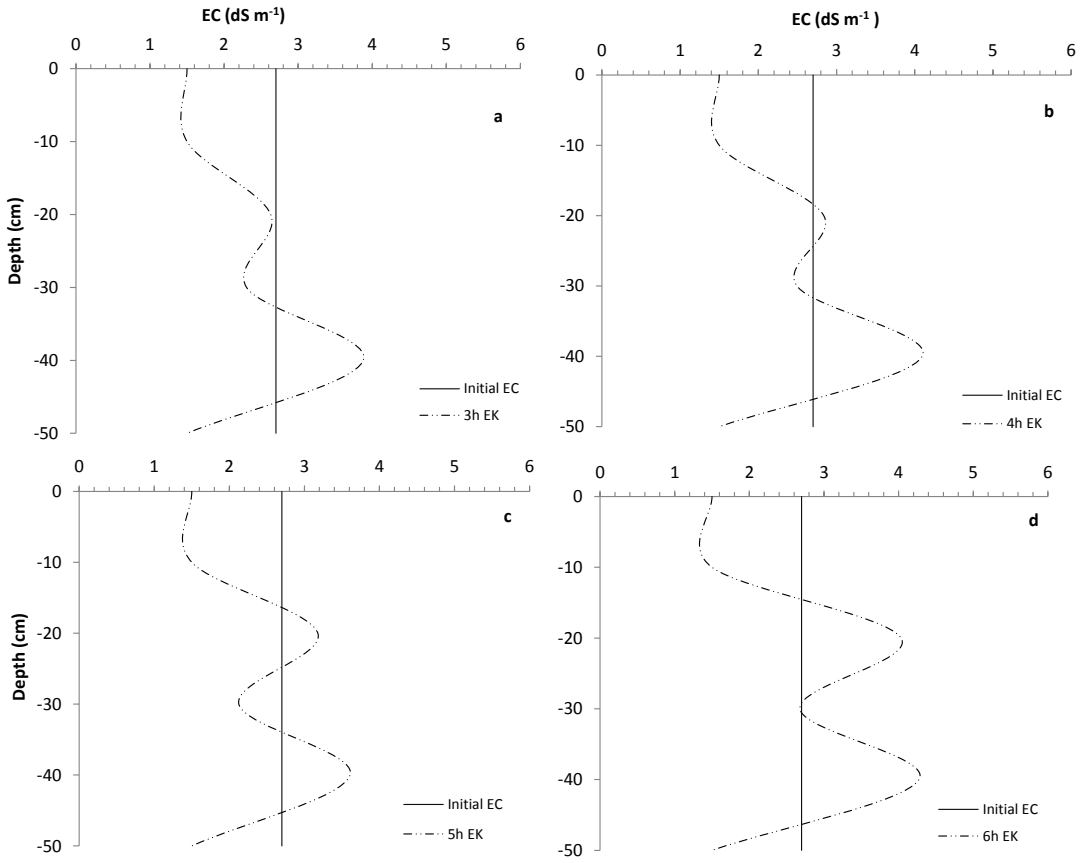

Figure 7-9: The predicted EC values with depth from running the DCEEM model to simulate applying EK for: (a) 3h, (b) 4h, (c)5h and (d)6h after 9h irrigation.

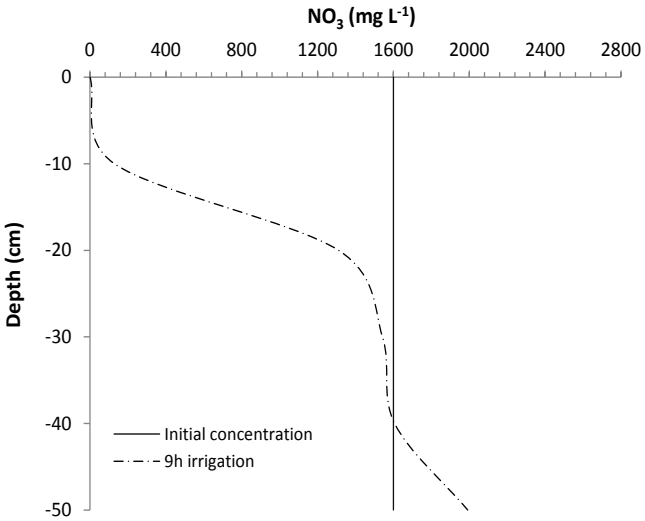

Figure 7-10: The predicted nitrate concentration with depth from running the DCEEM model 9 h 20 mL h^{-1} of irrigation without applying EK

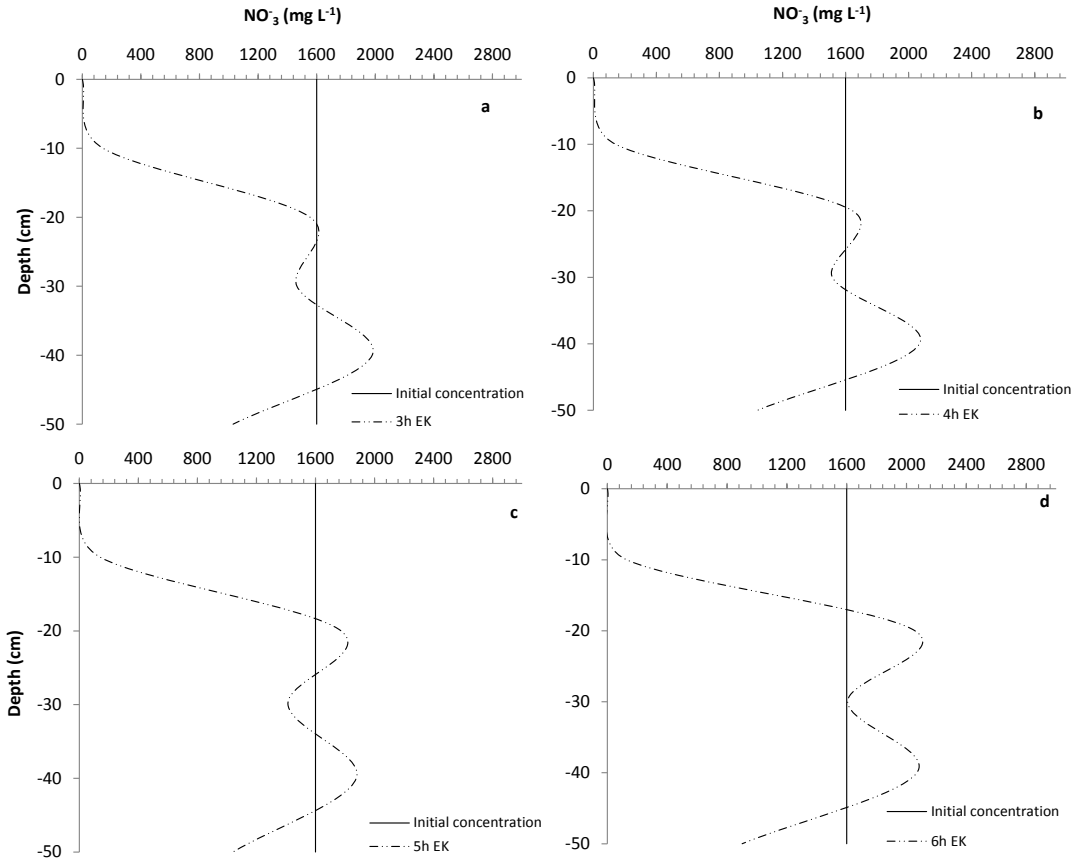

Figure 7-11: The predicted nitrate concentration with depth from running the DCEEM model to simulate applying EK for: (a) 3h, (b) 4h, (c)5h and (d)6h after 9h irrigation.

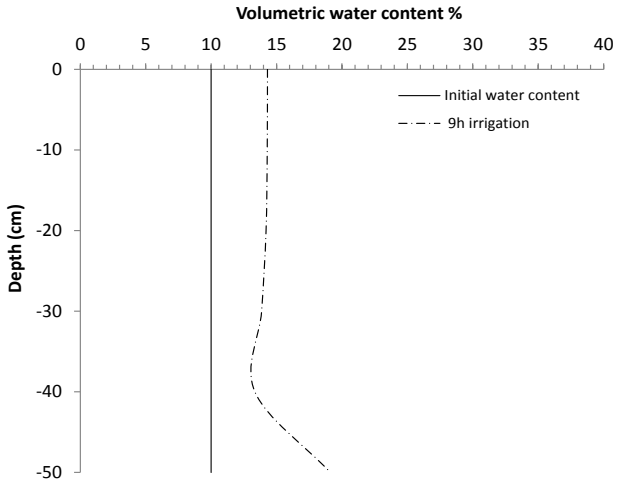

Figure 7-12: Volumetric water content with depth from running the DCEEM model 9 h 20 mL h^{-1} of irrigation without applying EK

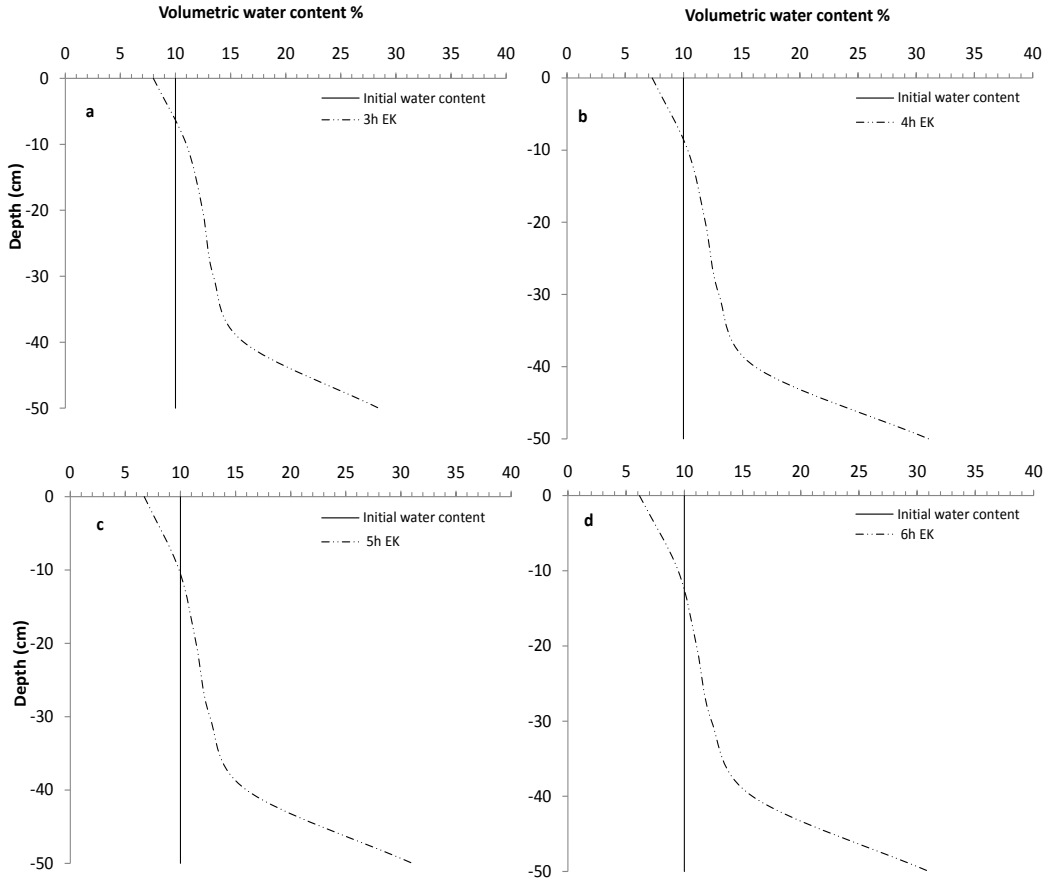

Figure 7-13: Volumetric water content with depth from running the DCEEM model to simulate applying EK for: (a) 3h, (b) 4h, (c)5h and (d)6h after 9h irrigation.

7.4.2.2 *Modelling dynamic solute changes within the profile with sequential EK and irrigation applications*

The DCEEM modelled application of sequential EK and irrigation applications showed substantial variations in nitrate concentration, EC and soil-water content at different depths throughout the sand columns (Figures 7-14 to 7-20). The model is clearly able to demonstrate differences in the nitrate concentration within the irrigated column when EK is either not applied (Figure 7-14) or applied (7-15). In particular, irrigation without EK (Figure 7-14) was shown to flush nitrate almost completely from the surface layers (0-20 cm) and to accumulate the nitrate at the bottom of the column (50 cm) during the 30 hour simulated treatment period. However, the model output (Figure 7-15) demonstrates that EK application produces electro-migration of nitrate upwards within the profile so that greater amounts of nitrate are retained in the upper column (particularly in the 0-20 cm depth interval). The model predicts (Figure 7-16) that the application of EK would produce a 0.8- to 1.2-fold increase in the total amount of nitrate retained in the 0-30 cm layers after 24 - 30 h of the treatments applied in this study.

The model outputs for EC (Figures 7-17 ad 7-18) and soil-water content (Figures 7-19 and 7-20) provide addition insight into the interaction of the physio-chemical processes occurring under irrigation and EK. When EK was not applied to the column, the model output shows (Figure 7-17) that downwards soil-water movement associated with the application of low EC irrigation water and drainage produces a decrease in the EC in the surface layers and an continuous increase to EC ~ 7 dS m^{-1} at 50 cm depth. However, with the application of EK (Figure 7-18), the rate of EC decline in the surface layers is reduced, the maximum EC within the profile is observed in the 10-20 cm layer and is more transient than in the no EK case.

By comparison, there are comparatively small differences in the soil-water contents observed between the no EK and EK applied management options (Figure 7-19 and 7-20). EK application reduced the surface (0 cm) volumetric soil water content by ~2% by the end of the EK application period but there were no substantial differences in soil-water content due to EK application at any depth by the end of the 30 h treatment period. This suggests that electro-osmosis does not play a significant role in soil-water (and solute) movement in the closed bottom irrigated columns with EK treatment, as simulated in this case. However, it is expected that this would be different in an open-bottom-column system that allowed free drainage (and leaching) below the target root zone. This inability to simulate an open bottomed column was a limitation of the current model, but there will realistically be a tension between nutrient leaching and the ability for EK to recover nitrate from below the bottom electrode in a system that can leach past the electrode depth.

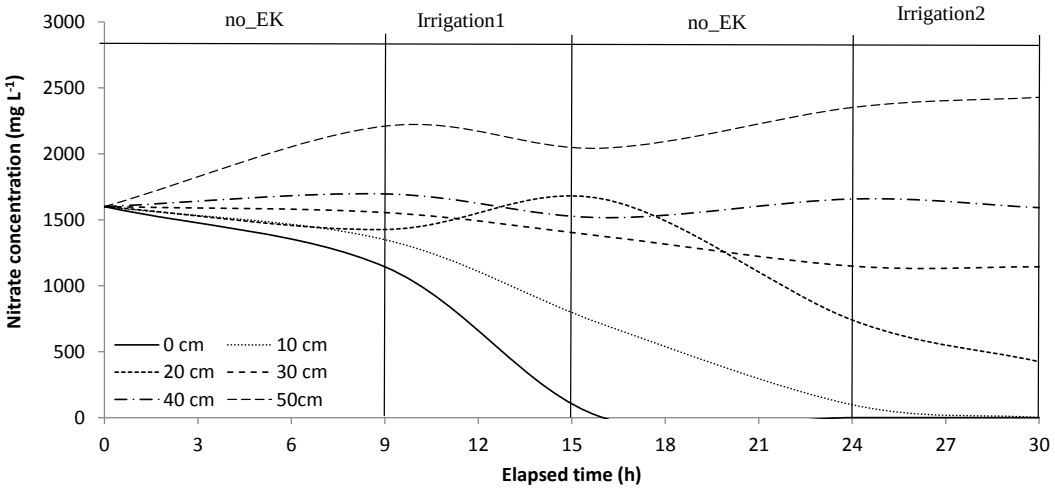

Figure 7-14: Effect of sequential periods of no-EK (i.e. drainage) and irrigation applications on nitrate concentrations predicted by DCEEM within a sand column

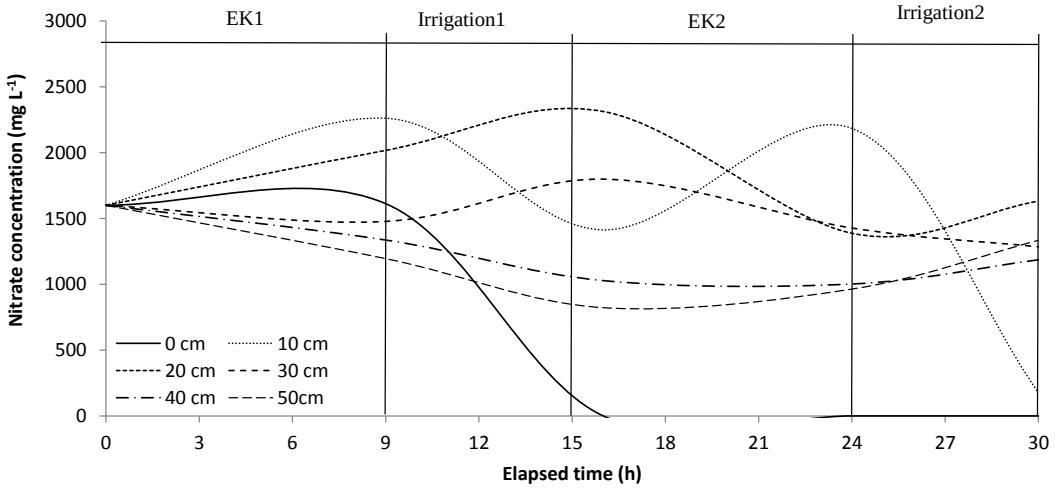

Figure 7-15: Effect of sequential EK and irrigation applications on nitrate concentrations predicted by DCEEM within a sand column

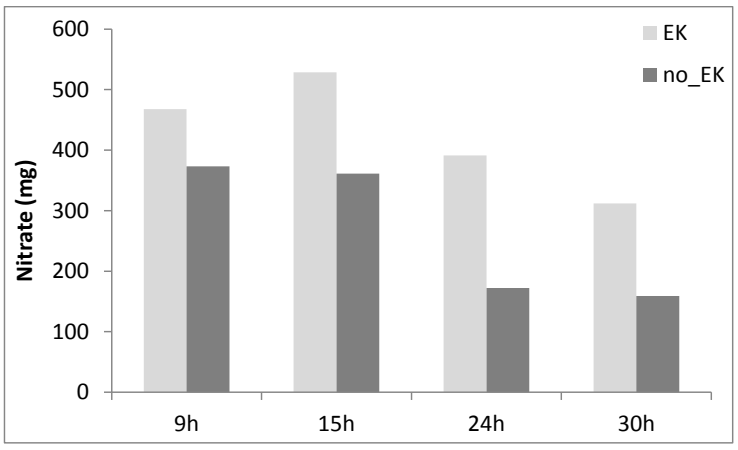

Figure 7-16: Total amount of nitrate in the 0-30 cm layer of the sand columns after the sequential applications of the EK, no-EK and irrigation treatments.

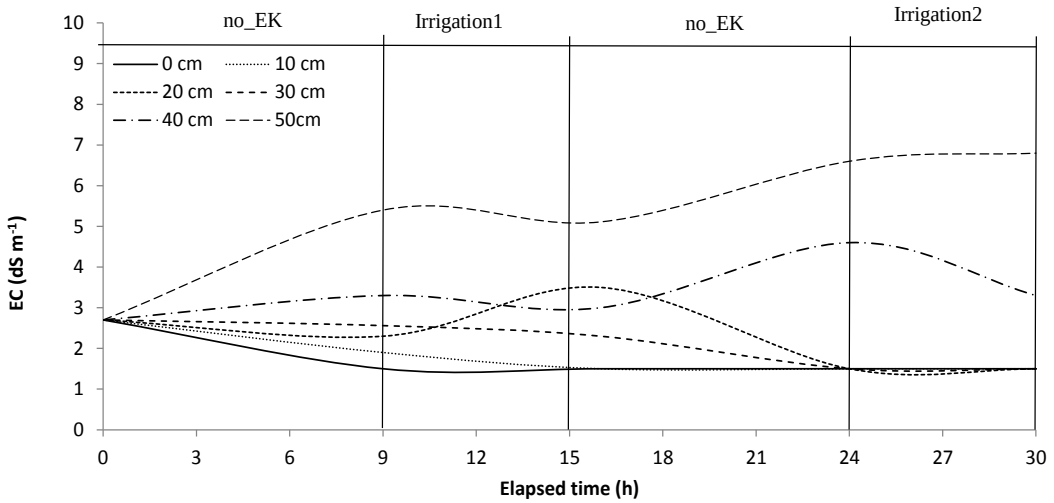

Figure 7-17: Effect of sequential periods of no-EK (i.e. drainage) and irrigation applications on EC predicted by DCEEM within a sand column.

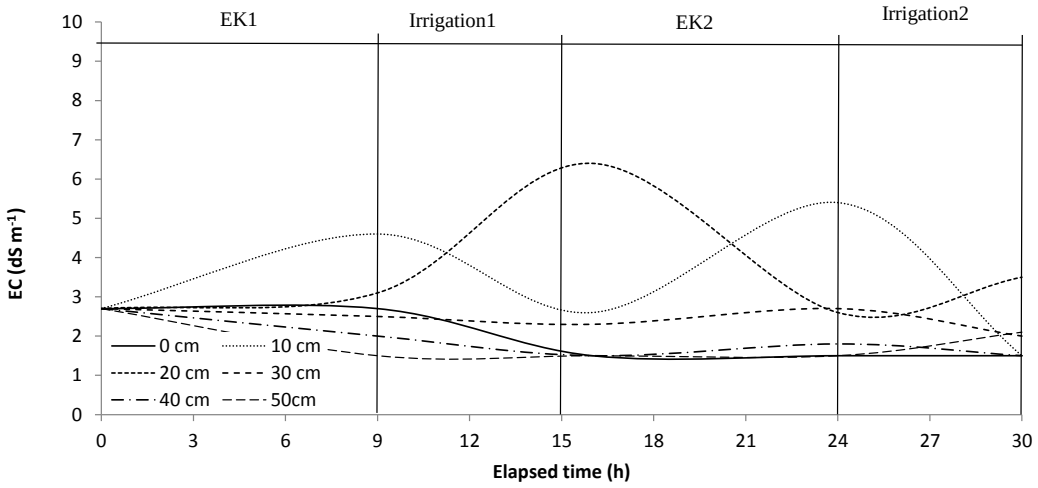

Figure 7-18: Effect of sequential EK and irrigation applications on EC predicted by DCEEM within a sand column

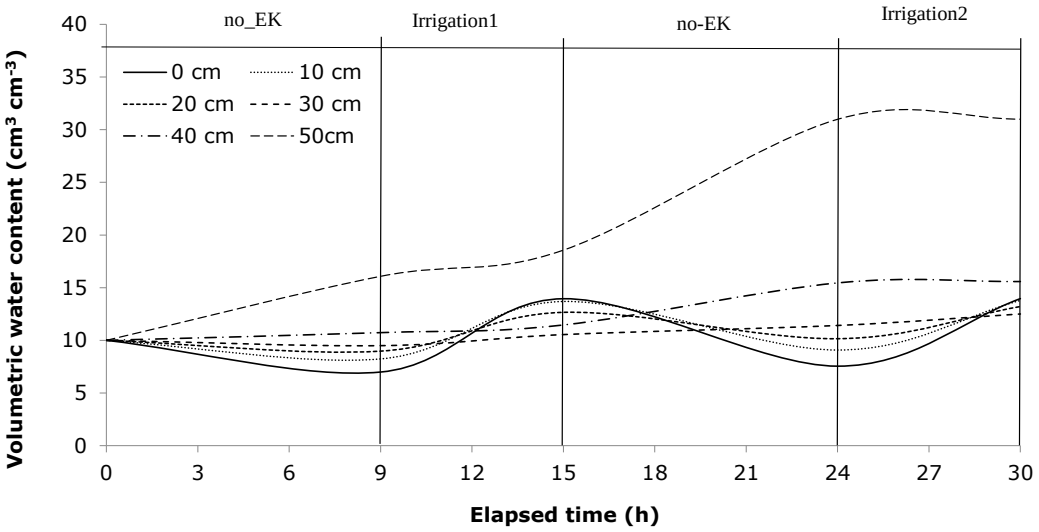

Figure 7-19: Effect of sequential periods of no-EK (i.e. drainage) and irrigation applications on soil water content predicted by DCEEM within a sand column

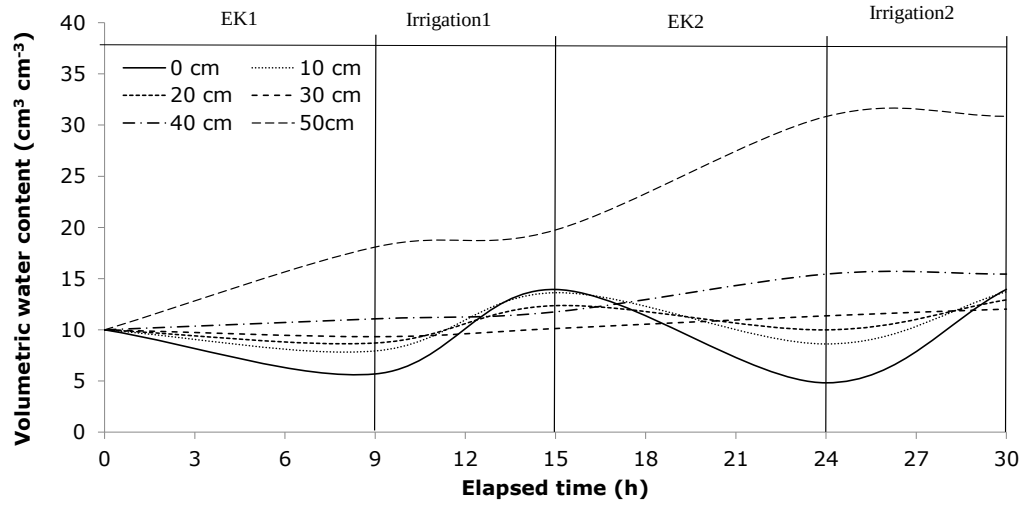

Figure 7-20: Effect of sequential EK and irrigation applications on soil water content concentrations predicted by DCEEM within a sand column

7.5 Conclusion

This chapter has outlined (Section 7.2) the development of a combined soil-water, solute movement and EK model to numerically describe soil-water and solute movement under the effect of gravitational and hydraulic potential gradients, concentration gradients, and electrical potential gradients induced by EK application. The combined "Diffusion Convection Electro-osmosis Electro-migration Model" (DCEEM) was shown (Section 7.4.1) to accurately describe the major phenomenon influencing soil-water and ion movement within a one-dimensional sand column. The validated DCEEM model was then used (Section 7.4.2) to simulate alternate EK and irrigation management strategies and demonstrate the effect of these management practices on EC changes, as well as soil-water and nitrate movement within irrigated sand columns.

The DCEEM modelled results produced for the demonstration case studies highlight the potential benefits of applying EK for the management of nutrients and ions in irrigated columns. While the current version of the model has limitations in relation to the selection of system design and management options, this work has demonstrated the utility of the model to better understand the relative scale and nature of the soil-water and ion movement interactions within the column. With further refinement, this model could be used to provide a basis for the development of EK management guidelines, visualisation of ion concentration changes within the columns, and for the optimisation of EK design and management practices in irrigated root zones.

Chapter 8: Conclusion and Recommendations

8.1 Introduction

This body of work has followed a linear progression, where each subsequent chapter builds upon the prior one. Hence, in this chapter, conclusions are drawn together from the study outcomes in order to facilitate a discussion of future recommendations. The study has evaluated the use of electro-kinesis (EK) for saline-sodic irrigation management in a simplified soil environment, as well as progressing the science toward prediction and subsequent application. This chapter then includes three main sections: Section 8.2 provides a review of the research; Section 8.3 concludes against the objectives of the study; and section 8.4 presents recommendations and future research.

8.2 Review of research

It has been established throughout the literature that there is need for increased food production to address the growing world population. Further, that irrigation has played, and will continue to play, a major role in supporting agricultural production, particularly in arid and semiarid regions of world. However, with a growing shortage of suitable water for agriculture, the focus has shifted towards exploring the feasibility of alternative sources of irrigation water such as saline-sodic groundwater and industrial effluent. Long-term use of untreated saline–sodic water for irrigation may adversely affect soil properties and crop yields.

Irrigation using marginally saline-sodic water can be managed, and this has traditionally been accomplished via the application of amendments to the irrigation water, or directly to the soil surface (for salinity) and by leaching, dilution and/or reverse osmosis (for salinity). The main idea behind these methods is to remove sodium from the soil and subsequently leach it from the root-zone, as well as to ensure that salt build up does not occur within the root-zone. However, irrigation water that is added to leach sodium and salts may lead to nitrogen loss. Thus, the identified need to develop an alternative method that reduces the sodium and salt accumulation, as well as limiting nitrogen loss. Electro-kinesis was identified as a developing technique for salt removal, with capacity to control nitrate movement. Thus, this research project evaluated, under laboratory conditions, the potential for EK to assist in managing salinity and nitrate movement in soils irrigated with saline water.

The main objectives in Chapters 4, 5, 6 and 7 of this dissertation were:

1) Evaluation of using electro-kinesis to control salt movement in an irrigated sand column.
2) An evaluation of the potential to use electro-kinesis for controlling nitrate movement in an irrigated sand column.
3) Using electro-kinesis to manage sodium and nitrate movement in a sand column irrigated with saline-sodic water.
4) Development of a numerical model to predict nitrate and salt movement in sand columns due to electro-kinesis and irrigation applications.

In undertaking this work, it was acknowledged early on that it would be useful to model how EK, solutes, nutrients and irrigation interact, as predictive capability was an identified knowledge gap. Hence, the DCEEM was developed throughout this work.

Objectives 1 and 2 provided data on modification movement, whilst Objective 3 demonstrated the expected interactions given irrigation, nutrient and EK dynamics. Objective 4 involved producing data to validate the core mechanisms of the model and to demonstrate how EK might be applied in an agricultural setting.

This work has subsequently produced insights and an evaluation into EK mechanisms and the potential to control sodium and nutrient movement for irrigated (simple) systems, as well making significant steps towards predictive capability. The work has presented a brief investigation, within the current DCEEM limitations, to inform best management considerations where irrigation and EK are to be used. However, the model and its use for optimising management decisions will need to be enhanced further (discussed in the recommendations section). Given work preceding this dissertation, and the work within it, it is envisaged that the immediate application of the EK irrigation technique might be small scale horticulture.

What follows are the specific conclusions drawn and recommendations from the work, expanding on that presented above.

8.3 General conclusion

8.3.1 Efficacy of EK to control sodium distribution and nitrate retention within root zones

The ability to use EK to control ion movement in a simplified soil solution was evaluated in laboratory experiments. The results were consistent with electro-migration theory. Anions (i.e. nitrate and chloride) were attracted towards the anode (surface) and cations (i.e. sodium) were attracted towards the cathode (bottom). For instance, sodium ions significantly accumulated in the base of the column (at 45 cm) when EK had been applied for ≥48 h. The distribution of the sodium ions was influenced by the rate of EK application with the minimum sodium concentration observed at 25 cm depth in the 0.01A EK treatment but at 35 cm depth in the 0.02 A EK treatment.

Similarly, application of EK to a simulated sand column was found to significantly affect nitrate retention and concentrations with depth. This movement was also influenced by both the duration and power of EK applied. Significant changes in nitrate concentration were apparent after 9 hours with the highest measured nitrate concentration extracted from 15 cm depth (7 cm below the anode). Irrigation, particularly after 9h, substantially reduced the nitrate concentration at the surface irrespective of whether EK was applied. However, applying EK after irrigation for a further 15 h led to increased nitrate concentration at depths <35. This result supports the application of EK after irrigation, and suggests that application of EK with irrigation is ineffective at retaining nitrate in high soil water conductivity environments.

In general, EK can be used to hold or move nitrate in the zone between the electrodes (i.e. in the 5 to 35 cm column layer in this work) and by increasing EK power and duration the effect is further increased. However, the application of EK (particularly at higher rates of application and longer durations) may also result in EC and pH conditions within the root zone which are not conducive to plant growth. Therefore, irrigation can be used to flush salts from the root zone and to buffer the root zone pH, albeit leaching nitrate out of the root zone simultaneously. This suggests that a

combination of irrigation and EK management practices could be used to reduce nitrate losses while managing salt concentrations within root zone.

8.3.2 Simultaneously managing sodium and nitrate for systems subject to irrigation and EK

The results obtained from chapter 6 showed that EK applications for saline-sodic irrigation can be managed to maintain a root zone suitable for a plant growth. This work concluded that while applying an electrical current led to an increase in nitrate concentration in the root zone and whiles a decrease in sodium concentration the adverse EC and pH affects could be controlled by irrigation and fertigation applications.

This study showed the possibility of using EK as a management option for controlling nitrate movement and minimising salt impacts in root zone. However, the dynamic nature of the changes in the root zone and time tag at each depth makes it difficult to identify optimal practices. Therefore, it was suggested that further work was required to evaluate numerous potential management options and that the development of a numerical model could allow optimisation for a particular set of management conditions.

8.3.3 Predicting solute dynamics and informing best management with EK

To enable evaluation of different EK and irrigation management options for the control of nitrate movement within the root zone a combined "Diffusion Convection Electro-osmosis Electro-migration Model" (DCEEM) model was developed and validated. The model was used to simulate alternate EK and irrigation management strategies and to demonstrate the effect of management practices on EC changes, soil-water and nitrate movement within irrigated sand columns. The results showed that the DCEEM model can be used to describe the soil-water and ion movement interactions within the column. However, the current version of the model needs further refinement to provide a basis for the development of EK management guidelines, visualisation of ion concentration changes within the columns, and for the optimisation of EK design and management practices in irrigated root zones.

8.4 Recommendations for further research

Recommendations for further research have been identified throughout the chapters. The key recommendations are outlined below.

8.4.1 Experimental and mechanistic aspects that require further investigation

8.4.1.1 *Low permeability media*

The efficiency of using EK to control solute movement in irrigated sand columns was investigated in the laboratory experiments of this work. Results obtained demonstrated that irrigation significantly reduced ion concentration in the surface depth for both the EK application and irrigation alone. The movement of ions was greatly affected by gravity and irrigation wetting front due to the fact sand has a high hydraulic conductivity. The main effect of EK application on soil-water movement seems to occur relatively quickly, and the model further predicts the majority of changes within 3 h of EK application and only minor changes in soil-water content thereafter with increasing EK application period.

However, solute movement in porous media is a function of the capillarity of the media, whereby the smaller the capillary the lower the flow rate and the higher the

internal suction of that void; i.e. slower drainage in terms of flow rate and greater volume of solution held under gravity. Hence, it could be expected that as clay content increases, and the pore size decreases due to packing of these micro-particles, that the effect of EK be magnified. Therefore, there is a need to test soils of numerous textures (i.e. clay: silt: sand ratios) in order to investigate this hypothesis and the associated effects on cations and anions.

8.4.1.2 *Media with charged surfaces*

Given that EK applies an electrical field to the simulated sand column and that clay has charged surfaces, the effect of EK needs to be tested for charged surfaces. In soils it is usual for the charge on clay to be negative and the cation exchange capacity (the capacity of this charge to attract cations) to be a vital component in controlling macro-nutrient dynamics. The cation suite held on the exchange complex strongly influences soil structural stability, whereby excess monovalent ions, predominantly sodium, but also potassium, can cause soil aggregates to disperse. This raises two interesting aspects: 1) how does mass movement of cations affect the structural stability of the soil; and 2) if soil clay is in a dispersed state and free to move, how does EK affect movement and entrainment? It is recommended that prior to EK being used for agricultural application that these postulates be understood thoroughly.

8.4.1.3 *Kinetics and dynamics of other solutes*

Although this study has demonstrated the ability of EK to remove excess sodium, as well as to control nitrate movement within a simulated sand column consisting of sand, further experimentation is needed on other solutes. As suggested above, the cation suite at the clay exchange is responsible for controlling soil structural stability. Hence, differential kinetics and dynamics of the major cations (calcium, magnesium, potassium and sodium) will be paramount to assessing this stability. Additionally, cations are a macro-nutrient source vital to plant production.

Furthermore, the various experiments in this current work have demonstrated that significant reductions and increases in pH are associated with EK application magnitude and duration. In acidic soil environments, aluminium and iron oxides are decreased resulting in iron and aluminium solubilising, which has ramification for crop production. Additionally, at alkaline pH in soil environments nutrient availability can be decreased and soil structure degraded due to calcium precipitation. Given that pH changes appear to be relatively rapid under EK, and revert similarly rapidly, the effect of these on oxide dissolution, nutrient availability and precipitation should be investigated.

In terms of these other solute dynamics (those other than sodium and nitrate), as was done in this work, it is recommended that dynamics be first investigated in a simplified system where non-charged medium is used. This will allow base mechanisms to be more easily incorporated into modelling applications.

8.4.1.4 *Effect on plant roots*

The results presented in this research are based purely on laboratory work using sand columns where by the depth of these columns was contrasted to investigate a root-zone. However, the effect of EK on plant root growth, solute uptake, and water access was not investigated. With respect to both the charged surface and other solutes recommendations above, it will be necessary to investigate these finding further, along with those in this dissertation, where plant roots are allowed to interact. This will be vital for agricultural application.

8.4.2 Model limitations and improvements

The DCEEM model in its current form couples the Huweg (2013) EK model with the ability to solve for the Richards Equation (Ross 1990) within a closed system. However, the current version of the model has limitations in relation to the selection of system design and management options. The base limitations have been reported in the Section 7.2.2., indicating the model requires further refinement.

8.4.2.1 *Base limitations and recommendations*

The base DCEEM limitations identified in Section 7.2.2 were:

- It is a one-dimensional model,
- Only fixed physical dimensions (50 cm length and 10 cm diameter) with a column mounted vertically and fixed electrode configuration (i.e. 5 cm anode and 45 cm cathode depth) can be simulated,
- The lower boundary condition is fixed (zero flux), disallowing root-zone leaching to be simulated,
- The surface boundary condition for irrigation is fixed water application rate and does not allow solute to be added (zero fertigation), and
- EK and water applications can only be evaluated sequentially, rather than simultaneous.

Additionally, the model (with the parameterisation used in Chapter 7) suggested a slight tendency to underestimate the effect of electro-osmosis on soil-water movement towards the cathode when EK is applied. This should be afforded further attention, although it was acknowledged that highly water conductive media, such as sand, that electro-osmosis did not appear to play a significant role in soil-water (and solute) movement in the closed bottom irrigated columns. Hence, understanding these mechanisms experimentally is going to be important to prioritising model aspect inclusion.

Building on these base limitations, the experimental and mechanistic recommendations above (Section 8.4.1) should also be considered as limitations to the current model that require further incorporation. In particular, the ability to model in a porous and structurally dynamic media will be of immense value.

Throughout this work it has become apparent that models such as APSIM (McCown et al. 1996) focus on the plant component with a simplified soil hydraulic-solute environment, whilst models such as HYDRUS (Simunek et al. 1996) focus on a complex soil hydraulic-solute environment, but incorporate simplified plant algorithms. An improved DCEEM model could be beneficially incorporated into both of these models. However a more efficient approach would be to couple these models.

8.4.2.2 *Optimising solute and nutrient movement*

The optimisation problem of nutrient retention and other solute management, particularly Na, is a complex problem. There is clear indication of an optimisation tension between factors, where not all factors can be optimal for any particular point in time. For example, this work has demonstrated it may not be possible to optimise EK applications for both soil solution sodicity and nitrogen concentration simultaneously. Further, irrigation effects on solute dynamics compounds issues associated with individual factor optimisation. Hence, without a modelling tool, such as the DCEEM, optimisation for desired system components will not be possible. Indeed, if the optimisation problem is undertaken manually, then changes in the system would be reactive and highly time consuming rendering the EK technique unfeasible

for practical application. Hence, future work, past the base limitations of the DCEEM identified in Chapter 7, need to focus on incorporating experimental and mechanistic limitations identified above, to allow for a practical optimisation approach on a case-by-case basis.

8.4.2.3 *Identification of practical application and limitation*

The recommendations provided above will allow for a better understanding of the effect of EK on soil physico-chemistry, and the ability to model this, but the scale of investigation to date has been laboratory only. The EK technique has previously been investigated for soil contamination treatment, dewatering biomass and the dewatering process of sludge (Bjerrum et al. 1967; Jeon et al. 2015; Kalumba et al. 2009; Lockhart 1983). However, field based agricultural investigations have not been conducted. The logistic and engineering limitations to field application require further investigation.

From the work in this dissertation, the most immediately identifiable application for EK would be in small scale hydroponics with non-charged-surface media. Increasing the scale of investigation from small column, to a pot and full-scale hydroponic level could provide for a practical application useful for simultaneously investigating the experimental and mechanistic recommendations identified above.

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1. Appendix A DCEEM description and numerical details

A.1 Electrical equations

The vertical soil column is divided into N segments of equal length Δz as shown in Figure A-1. Based on Kirchhoff's current law, the continuity condition of the current density J is given by

$$\nabla J = 0 \qquad \textbf{Equation A-1}$$

where $\nabla = \partial / \partial z$ (for 1D model); z is the vertical coordinate and positive upward; and

$$J = \frac{I}{A} \qquad \textbf{Equation A-2}$$

in which I is the constant electrical current; and A the cross-sectional area of the soil column

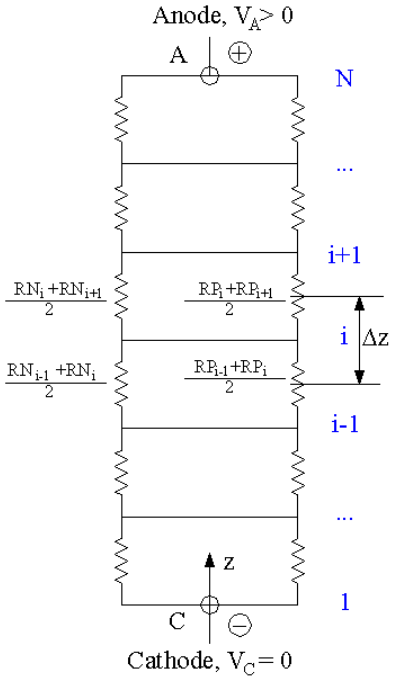

Figure A1-1:One-dimensional electrical model for a soil column.

The i^{th} segment has resistances RN_i and RP_i. Thus its conductances GN_i and GP_i are given by

$$GN_i = \frac{1}{RN_i} = \frac{A\sigma_{ni}}{\Delta z} \qquad \textbf{Equation A-3a}$$

$$GP_i = \frac{1}{RP_i} = \frac{A\sigma_{pi}}{\Delta z} \qquad \textbf{Equation A- 3b}$$

where σ_{ni} and σ_{pi} are electrical conductivity (EC) at node i due to the anion (negative ion) and cation (positive ion) electro-migration, respectively.

From Figure A1-1, the negative and positive electrical conductance of the segment (*i-1,i*) are:

$$GN_{i-1,i} = \frac{2}{RN_{i-1} + RN_i} = \frac{2GN_{i-1}.GN_i}{GN_{i-1} + GN_i} \qquad \textbf{Equation A-4a}$$

$$GP_{i-1,i} = \frac{2}{RP_{i-1} + RP_i} = \frac{2GP_{i-1}.GP_i}{GP_{i-1} + GP_i}. \qquad \textbf{Equation A-4b}$$

The total electrical conductance of the segment (*i-1,i*) is:

$$G_{i-1,i} = GN_{i-1,i} + GP_{i-1,i} = \frac{2GN_{i-1}.GN_i}{GN_{i-1} + GN_i} + \frac{2GP_{i-1}.GP_i}{GP_{i-1} + GP_i}. \qquad \textbf{Equation A-5}$$

Thus the total electrical resistance of the segment (*i-1,i*) is:

$$R_{i-1,i} = \frac{1}{G_{i-1,i}}. \qquad \textbf{Equation A-6}$$

The total resistance of the soil column from the anode to the cathode is:

$$R_{ac} = \sum_{i=2}^{N} R_{i-1,i} \qquad \textbf{Equation A-7}$$

where *N* is the number of nodes in the soil column. The current in the segment (*i-1,i*) is:

$$I_{i-1,i} = G_{i-1,i}\left(V_i - V_{i-1}\right) \qquad \textbf{Equation A-8a}$$

where V_i is the voltage at node *i*. Similarly, the current in the segment (*i,i+1*) is

$$I_{i,i+1} = G_{i,i+1}\left(V_{i+1} - V_i\right). \qquad \textbf{Equation A-8b}$$

Making use of (Equation A1-1) and (Equation A1- 2) results in

$$I_{i-1,i} = I_{i,i+1}. \qquad \textbf{Equation A-8c}$$

or

$$G_{i-1,i}\left(V_i - V_{i-1}\right) - G_{i,i+1}\left(V_{i+1} - V_i\right) = 0 \qquad \textbf{Equation A-9}$$

From (Equation A-9) we can construct a system of equations as follows.

$$\mathbf{G}.V = RHS \qquad \textbf{Equation A-10}$$

A.2 An electrical model to determine average anionic and cationic mobilities

In this section, the electrical model developed in Huweg (2013) is used to determine average anionic and cationic mobilities (K_n and K_p). The model is briefly described as follows. Consider a soil column as shown in Figure A1-2a. When a difference of

voltage between the anode and cathode is applied, the concentration front will move from the cathode to the anode. There is a surface at the concentration front, called the depletion surface. This surface divides the soil domain into two regions including the high conductivity region near the anode and the depletion region near the cathode as shown in Fig. A-2a. In DCEEM, some simplifying assumptions are made: (i) The cathode is effectively washed. This means that the cathode accumulation region is non-existent. (ii) All anions reaching the anode exit the soil column, for example, as chlorine gas (Cl_2) in the case of [Cl^-] ions. This means that the anode accumulation region is non-existent. (iii) There is no soluble anion in the depletion region. This means there is no anionic current. Therefore, the cation concentration throughout the depletion region remains uniform and constant with time. (iv) Chemical reactions occur only at the electrode surfaces.

Figs. A-2(b-d) show three thin soil slices in the soil column. Generally, the current flow in an ionic environment is a combination of anionic and cationic currents. This is indeed the situation for the high conductivity region as illustrated in Fig. A-2b. In this case of the high conductivity region, the cationic charge entering any soil slice from the anode side in a given time interval (Δt) is equal to the cationic charge leaving the slice on the opposite side during that time. A similar explanation can be made about the anionic charge entering and leaving the slice. Therefore, it can be concluded that the current flow does not alter the volumetric concentration of anionic and cationic charges in the high conductivity region.

As illustrated in Fig. A-2d, the situation is similar in the depletion region, except that the total current is due to the cationic flow only. The conclusion that the current flow does not alter the volumetric concentration of anionic and cationic charges still applies.

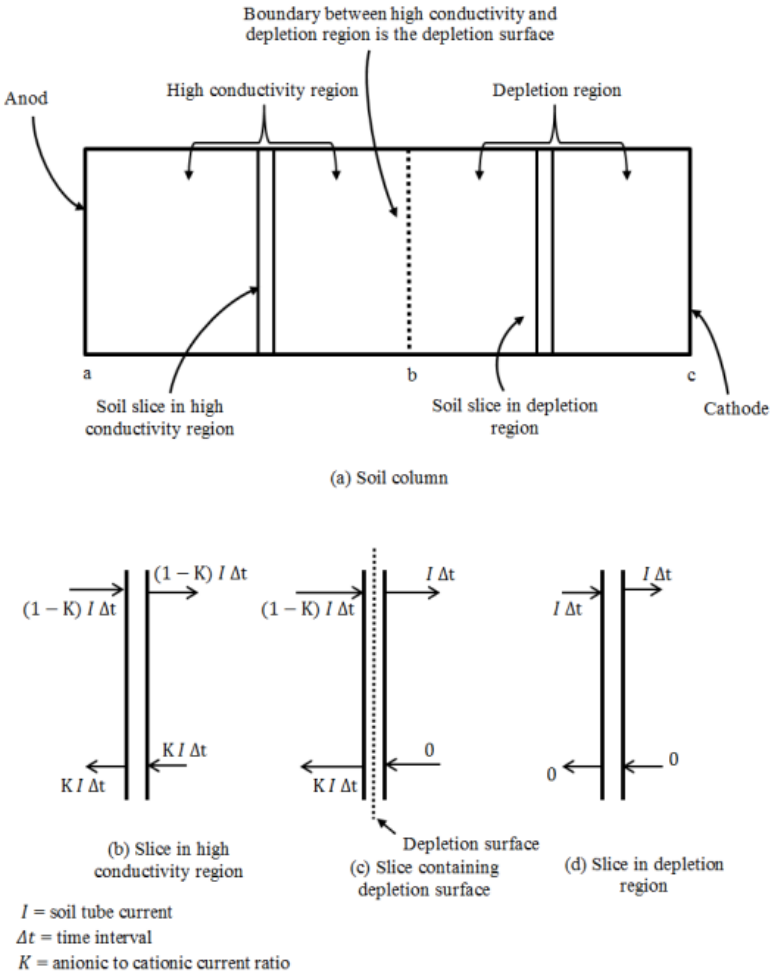

Figure A-2: The depletion surface (from Huweg, 2013)

The situation is significantly different for a thin soil slice containing the depletion surface. As illustrated in Figure A-2c, equal but opposite spatial discontinuities exist in the cationic and anionic current flows. These discontinuities result in the boundary between the high conductivity region and the depletion region shifting towards the anode at a speed given by:

$$S = \frac{KJ_t}{C_h - C_m}$$ **Equation A-11**

where J_t is the current density (A/m^2); and the ratio K is given by

$$K = \frac{I_n}{I_n + I_p} = \frac{\Delta VG_n}{\Delta VG_n + \Delta VG_p} = \frac{\sigma_n}{\sigma_n + \sigma_p} = \frac{\sigma_n}{\sigma_h}$$ **Equation A-12**

in which σ_h is the pre-treatment soil EC.

Therefore,

$$\sigma_n = K\sigma_h$$ **Equation A-13a**

$$\sigma_p = \sigma_h - \sigma_n .$$ **Equation A-13b**

Given the value of K, J_t and the speed of the concentration front S, from (Equation A-11) we have

$$C_h - C_m = \frac{KJ_t}{S}. \qquad \textbf{Equation A-14}$$

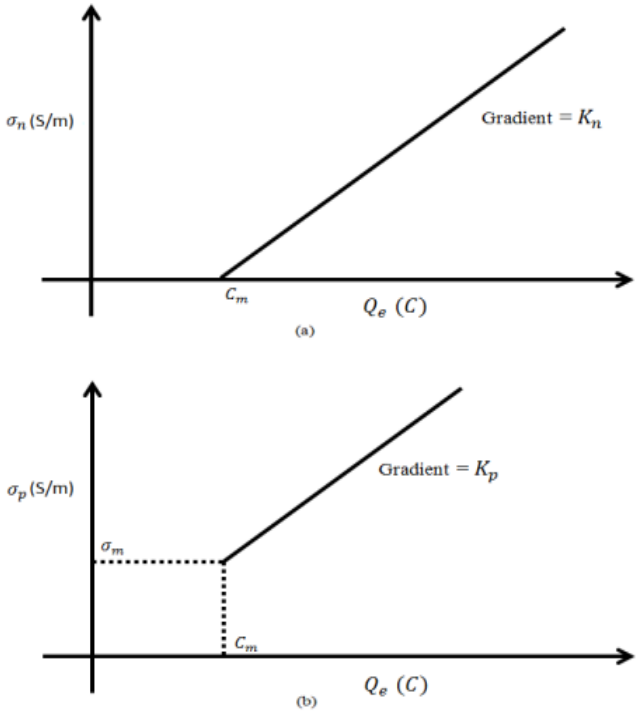

Figure A1-3: Effective mobilities (from Huweg, 2013)

In this model, instead of estimating individual mobilities for all ionic species in the soil sample, the effective anionic and cationic mobilities (K_n and K_p) are calculated. Based on Figure A-3, the effective mobilities are determined as:

$$\sigma_n = K_n\left(C_n - C_m\right)$$
$$\sigma_p = K_p\left(C_p - C_m\right) + \sigma_m \qquad \textbf{Equation A-15a, Equation A-15b}$$

where σ_m is the minimum soil EC (post-treatment soil EC).

So,

$$K_n = \frac{\sigma_n}{C_h - C_m},$$
$$K_p = \frac{\sigma_p - \sigma_m}{C_h - C_m} \qquad \textbf{Equation A-16a, Equation A-16b}$$

where σ_n, σ_p and $C_h - C_m$ are calculated using (**Equation A-13a**), (**Equation A-13b**) and (**Equation A-14**), respectively.

A.3 **Governing equation for fluid movement in soil**

The governing equation for fluid motion in soil under hydraulic and electric fields are written as (Yeung,1993; Celia and Bouloutas, 1990):

$$\frac{\partial \theta}{\partial t} = -\nabla q \qquad \textbf{Equation A-17}$$

where the water flux q is driven by the hydraulic and electric gradients,

$$q = q_h + q_e \qquad \textbf{Equation A-18a}$$

in which

$$q_h = -K(h)\left(\nabla h + 1\right), \qquad \textbf{Equation A-18}$$

$$q_e = -K_e \nabla V \qquad \textbf{Equation A-18c}$$

where h is pressure head [m]; θ the moisture content [m^3 m^{-3}]; $K(h)$ the unsaturated hydraulic conductivity [m s^{-1}]; and K_e the electroosmotic permeability coefficient (m^2/V.s).

The unsaturated soil hydraulic properties and are highly nonlinear functions of pressure head. Van Genuchten (1980) proposed an analytical model, namely Mualem-van Genuchten model, for the hydraulic properties as follows.

$$\theta = \begin{cases} \dfrac{\theta_s - \theta_r}{\left(1 + \left(\alpha |h|\right)^{\eta}\right)^{\mu}} + \theta_r & if \;\; h \le 0 \\ \theta_s & if \;\; h > 0 \end{cases} \qquad \textbf{Equation A-19a}$$

$$K = \begin{cases} K_s S_e^L \left[1 - \left(1 - S_e^{\frac{1}{\mu}}\right)^{\mu}\right]^2 & if \;\; h \le 0 \\ K_s & if \;\; h > 0 \end{cases} \qquad \textbf{Equation A-19b}$$

where θ_r and θ_s are the residual and saturated water content, respectively; K_s the saturated hydraulic conductivity; α the inverse of the air-entry value; η the pore-size distribution index; L the pore-connectivity parameter; S_e the effective water content given by:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}; \text{ and}$$

$$\mu = 1 - \frac{1}{\eta}, \eta > 1.$$

The above equations contain six independent parameters: $\theta_s, \theta_r, \alpha, \eta, \mu$ and L. The pore-connectivity parameter L was estimated to be about 0.5 as an average for many soils (Mualem 1976).

A.4 Governing equation for solute transport in soil

The solute transport in soil is governed by (Rowe, 1996; Yeung, 1993; Eid, 2000; Li, 2011):

$$Rd\frac{\partial C}{\partial t} = -\nabla(J_d + J_c + J_e) \quad \textbf{Equation A-20}$$

where C is the contaminant concentration; and

$$Rd = \frac{\theta + \rho K_d}{\theta} \quad \textbf{Equation A-20a}$$

in which K_d is the distribution coefficient; and ρ the dry bulk density of the soil; and

$$J_d = -D_e \nabla C \quad \textbf{Equation A-21a}$$

$$J_c = v_a C \quad \textbf{Equation A-21b}$$

$$J_e = K_e C \nabla V \quad \textbf{Equation A-21c}$$

in which D_e is the effective diffusivity in soil (m^2/s); and the average pore-water velocity is defined by

$$v_a = \theta q \quad \textbf{Equation A-21d}$$

where q is the water flux due to hydraulic gradient and electro-osmosis calculated by Equation A-18a.

A.5 Boundary conditions

The boundary conditions for the voltage are:

$$V(z_1) = 0 \quad \textbf{Equation A-22a}$$

$$V(z_N) = V_A \quad \textbf{Equation A-22b}$$

where V_A is the anode voltage.

The anionic and cationic currents are assumed to be continuous through the anode. Thus,

$$\frac{\partial C_p(z_N)}{\partial t} = 0 \quad \textbf{Equation A-23a}$$

$$\frac{\partial C_n(z_N)}{\partial t} = 0. \quad \textbf{Equation A-23b}$$

And, no anion enters or is generated at the cathode. Thus the negative ionic concentration at the cathode must satisfy the following condition

$$\frac{\partial C_n(z_1)}{\partial t} = 0 \qquad if\ \sigma_n = 0 \quad \textbf{Equation A-24a}$$

$$\frac{\partial C_n(z_1)}{\partial t} = -\nabla J \ if \ \sigma_n > 0 \, . \qquad \textbf{Equation A-24b}$$